FUNDAMENTAL SYNTHETIC FUEL STABILITY STUDY. FIRST ANNUAL REPORT, MAY 1, 1979-APRIL 30, 1981

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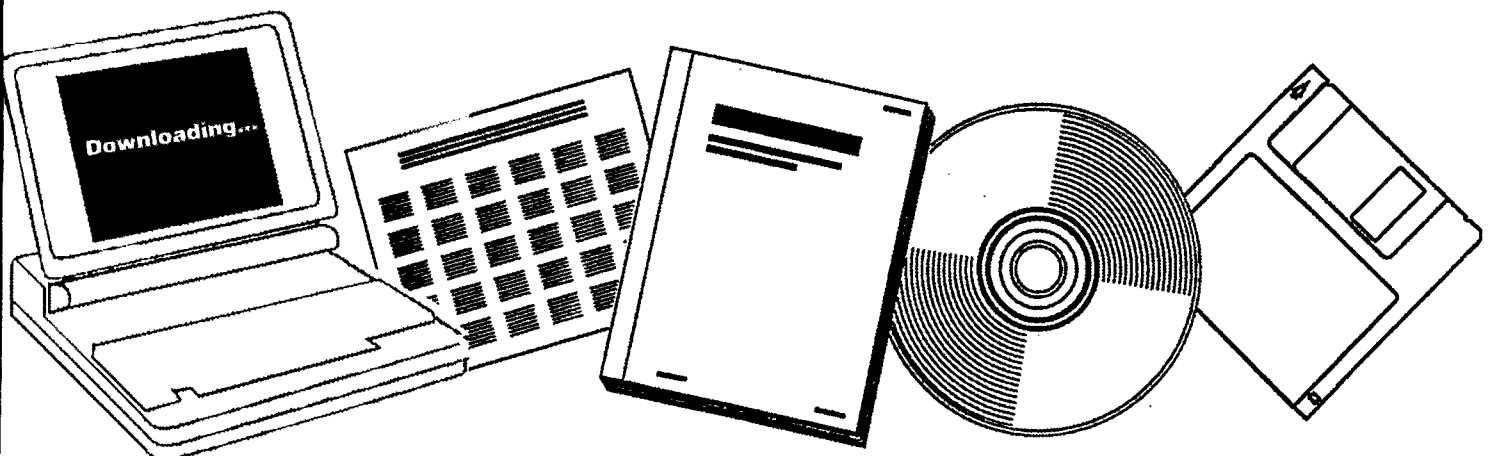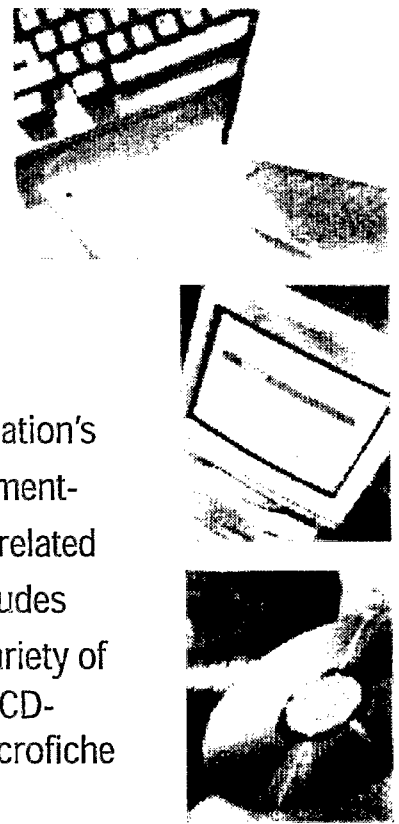
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FUNDAMENTAL SYNTHETIC FUEL STABILITY STUDY

First Annual Report
May 1, 1979—April 30, 1980

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U.S. DEPARTMENT OF ENERGY

PREFACE

This report was prepared by Exxon Research and Engineering Company, Linden, New Jersey, for the Department of Energy under Contract DE-AC19-79-BC10045. The program was monitored by Dr. Dennis W. Brinkman of the Bartlesville Energy Technology Center.

The report covers the initial year's effort over the period from May 1, 1979 to April 30, 1980. The principal investigators were Dr. John W. Frankenfeld and Dr. William F. Taylor assisted by Mr. Robert L. Bruncati.

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SUMMARY

This report covers the first year of a multi-year program to study the effects of nitrogen compounds on the storage stability of synthetic fuels derived from oil-shale and coal. A variety of organic nitrogen compounds were evaluated for their tendencies to promote sediment in hydrocarbon fuels under accelerated storage conditions. Three types of diluents were employed which represented fuels of increasing complexity. These were pure n-decane, petroleum derived JP-8 and No. 2 diesel fuel. The fuels and fuel mixtures were stored at 110°F (43.3°C) and 150°F (65.5°C) in the dark. Sediment formation was determined gravimetrically.

A literature search was performed in order to determine the state of the art of storage stability with synthetic fuels and to identify the most prevalent nitrogen, sulfur and oxygen compounds found in shale and coal derived middle distillate fuels.

The effects of nitrogen compounds on sediment formation, observed previously in pure hydrocarbon systems were confirmed in broad range fuels. The most deleterious species to fuel stability were found to be alkylated heterocyclic nitrogen compounds. The most reactive compounds were those with two or more alkyl groups, at least one of which was situated on a carbon adjacent to the nitrogen. A typical, highly deleterious, compound which was studied extensively is 2,5-dimethyl-pyrrole (DMP). Other nitrogen compounds, such as amines, amides and non-alkylated heterocycles were non-deleterious when tested by themselves. However, several of these apparently harmless species were found to interact with deleterious nitrogen compounds to promote sediment formation.

With the exception of sulfonic acids, none of the sulfur or oxygen compounds studied produced sediment when tested by themselves.

However, some of them interacted with nitrogen compounds to either enhance (carboxylic acids) or retard (aromatic thiols) sediment formation.

The nature of the diluent had a significant effect on sedimentation rate, with the most complex medium (No. 2 diesel) producing the most, and the simplest (pure n-decane) the least sediment with the same nitrogen compound under identical storage conditions. It is not yet known whether this is due to solvent effects or to the presence of trace impurities in the more complex fuels.

Dissolved oxygen was found to promote sediment formation to a significant degree.

The sedimentation reaction with 2,5-dimethylpyrrole (DMP) followed the Arrhenius equation for temperature dependence. The apparent activation energy is in the range of 10-15 kcal/mole.

During the course of this work a modified storage stability test was developed which significantly improved the accuracy of sediment determinations.

1. INTRODUCTION

Both the U.S. and world petroleum reserves are being depleted at a rate that can no longer be ignored. As a result, the development of alternate fuel sources is a virtual necessity within a few decades. Two of the most promising new sources are oil shale and coal.[1] Although processes are available for the production of synthetic liquids from shale and coal, the investment costs associated are very large and the fuels produced will unquestionably be significantly different in chemical composition from present day petroleum-derived materials. Comparisons of some average properties of crude oils derived from various sources are shown below:[1]

		Petroleum	Shale Liquid	Coal Liquid
Carbon	%	83-87	81	78-85
Hydrogen	%	11-15	10	7.5-10.0
Oxygen	%	0.5-5.0	6	7-11
Nitrogen	%	0.1-0.5	1-3	0.6-2.0
Sulfur	%	0.6-6.0	0.6-3	0.3-2.0

A major difference in composition in crudes from various sources is the nitrogen content. It is known that organic nitrogen compounds can be deleterious to fuel quality especially with respect to stability. However, the causes and the magnitude of the problems are not well defined. This is due to the fact that the nitrogen content of nearly all petroleum-based fuels is too low to present serious concern. The situation is quite different with synthetic fuels where nitrogen levels can reach 3%. A major emphasis in this project is to study the nitrogen problem in depth in order to assess its impact on future synthetic fuel processing.

1.1 PROGRAM OBJECTIVE

The overall objective of this program is to develop a comprehensive synthetic fuel stability technology base by extending our knowledge of the effect of the chemical composition and physical properties of petroleum fuels on storage and thermal stability to future shale oil and coal derived fuels. This fundamental base will provide longer term synthetic fuel stability technology which can be used for tradeoff assessments such as fuel stability versus refining/upgrading severity or to define compositional goals for new or broadened specification fuels.[1] In addition, the study has the following specific, long-term objectives which extend beyond the current contract period:

- Extend the study of the effects of various nonhydrocarbon impurities, particularly nitrogen, sulfur and oxygen containing compounds and metals on sediment formation and thermal stability to determine which species are deleterious and at what levels.

- Determine the effects of certain storage conditions on fuel stability.

- Extend studies in model systems to actual synthetic liquids, such as those derived from shale and coal liquids.

- Determine effects of certain processing conditions on storage and thermal stability of actual synthetic liquids.

- Summarize effects of fuel composition and/or processing techniques on stability characteristics of synthetic fuels; develop comprehensive technology base for future trade-off analyses.

1.2 GENERAL METHOD OF APPROACH

In order to meet the objectives detailed above in a systematic way, a multi-year program has been undertaken in which each year or phase serves as a "building block" for the succeeding phase. This "building block" approach is outlined in Figure 1. The program began with a study

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FIGURE I

Past & Present Exxon & BETC Research Interaction
of Various Studies with Present Program

- OTHER PROGRAMS

PRESENT PROGRAM

OTHER PROGRAMS

Alternate Fuel
Chemistry

(U. S. Navy)

Techniques; →
Cpds. to study;
storage parameters
identified.

I. MODEL FUEL STORAGE
STABILITY

U. S. Govt.
techniques

mechanisms
assessments

Bartlesville
Energy Techno-
logy Center Fuel
Stability Pro-
grams

Techniques; Mechanisms
Assessments

High Stability
Fuel

(U. S. Navy)

Apparatus; →
Techniques; cpds.
to study.

II. MODEL FUEL THERMAL
STABILITY

Mechanisms

Important
parameters
to study.

Study of Hydro-
carbon Vapor
Deposits

(U.S. Airforce)

Sample Characteristics
Analytical Methods
Processing techniques

Low Temperature
Properties of
Diesel Fuels
(DOE)

Samples; →

Additives to
consider.

III. SHALE LIQUID STUDIES

IV. RECOMMENDED PROCEDURES

Evaluation of
Methods to pro-
duce aviation
turbine fuels
from synthetic
crude
(U.S. Airforce)

Processing
techniques;
Fuel characteris-
tics; cost consi-
derations

Future Synthe-
tic Fuels

(U.S. Army)

of model compounds in pure hydrocarbons and is progressing through more and more complex fuel systems until it culminates in a study of actual synthetic fuels derived from shale or coal. By so doing, a thorough understanding of the effects of fuel composition on stability will be developed which can serve as a basis for the selection of future processing schemes which afford acceptably stable fuels in economically feasible ways.

2. TECHNICAL DISCUSSION

2.1 TASKS TO BE PERFORMED

The objectives outlined were accomplished by performing the following tasks:

(1) Survey and assessment of previous work impacting on the present study.

(2) Extend the study of trace impurities especially nitrogen compounds on storage stability of model fuels.

(3) Study of the interactions between trace impurities.

(4) Study effects of hydrocarbon composition and boiling range.

(5) Study effects of water, light and dissolved oxygen.

2.2 MATERIALS AND METHODS

2.2.1 Test Fuels

Two test fuels were employed. These were a jet fuel from the Bayway, New Jersey Refinery (an additive-free jet fuel meeting specifications of JP-8) and a No. 2 diesel fuel from the Baytown, Texas refinery. Inspections on these fuels are given in Table 1. Most work described in this report was done using No. 2 diesel as the diluent.

2.2.2 Test Compounds

Test nitrogen, sulfur and oxygen compounds were purchased from commercial sources. Where necessary these were purified by distillation or crystallization.

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2.2.3 Accelerated Storage Stability Test[a]

The test fuels were filtered through glass wool, followed by
a medium fritted disc filter immediately before use. Each additive was
weighed into a clean, tared, 500 ml pyrex Erlenmeyer flask fitted with
a ball joint stopper. To this was added 300 ml of the test fuel.
Duplicate samples were made up as well as additive-free samples. All
samples were stoppered and stored in darkness at 110°F $\pm$ 2°F (43.3°C),
150°F $\pm$ 2°F or at ambient temperature for a specific period. The time
periods of 14-days, 28-days and 56-days were chosen as "standard".
In a few cases, longer and shorter periods were also employed. After storage
the contents of the flask were filtered rapidly through a tared 55 mm Buchner
funnel with a glass filter pad. The filtrate was stored in brown bottles
under refrigeration for further use. The Erlenmeyer flasks and the filter
cakes were washed with a small amount of reagent grade isooctane and the
washings filtered and then discarded.[c] The flasks and the Buchner funnels
were dried in a vacuum oven (pump) at 120°C for 1-1/2 hours, allowed to cool
under vacuum and weighed. This resulted in two sediment weights:[d,e]

$$(1) \quad \text{Insoluble sediment} = \frac{\text{Weight of Buchner} - \text{Tare}}{300} \text{ mg/100 ml}$$

$$(2) \quad \text{Adherent sediment} = \frac{\text{Weight of Erlenmeyer} - \text{Tare}}{300} \text{ mg/100 ml}$$

(a) This method is a modification of that used by Brinkman, Whisman and
Bowden, "Stability Characteristics of Hydrocarbon Fuels from Alternate Sources", BETC/RI-78/23 (1979).
(b) All filtrates were analyzed by color by ASTM D1500; "max" for this was 5.0.
(c) This can be omitted for light fuels such as gasoline or some jet fuels.
(d) Blank corrections, obtained by applying the same measurements to the fuel without additives, are subtracted from each weight.
(e) A total sediment weight, the sum of (1) and (2) is also reported; this is, perhaps, the most useful measurement.

TABLE 1

INSPECTIONS ON TEST FUELS

	No. 2 Diesel	JP-8[a]
API Gravity 60/60	35.8	41.3
Specific Gravity	0.8458	0.8189
Color (ASTM D1500)	0.5	0.0
Viscosity (C_{ST}/100°F)	3.02	1.62
Acid No. (ASTM D664)	.03	0[b]
Existent Gum (Steam Jet)		1.0 mg/100 ml
Wt.% S	0.19	703 ppm
Wt.% N	40 $\pm$ 10 ppm	5 $\pm$ 1 ppm
Hydrocarbon Type		
Saturates, %	76.0	82.6
Aromatics, %	23.0	17.2
ASTM Distillation		
IBP	281	251
10%	397	342
20%	433	375
30	464	394
40	492	415
50	520	430
60	547	448
70	573	465
80	602	483
90	632	504
FBP	684	548

[a] Sample was a commercial Jet A which is equivalent to an additive-free JP-8.

[b] No titer obtained.

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2.3 LITERATURE REVIEW

A literature review was conducted using the key words and descriptors shown in Table 2. Chemical Abstracts and NTIS were searched. Table 3 gives the number of citations for each descriptor level. Thus, when only shale or shales was searched, over 4,000 references were obtained from Chemical Abstracts and over 1,000 from NTIS. When the additional restriction of a fuel term was added the citations fell to 463 and 324, respectively, and with the further restriction of some stability term only 49 and 43 were elicited. This is indicative of the current paucity of references to the deterioration of actual shale liquids. The most pertinent references for this project are given in the Appendix.

TABLE 2

Key Words and Descriptors Used in Literature Review for Shale(a)

A. Source	B. Fuel Type	C. Descriptors
Shale	Derived	Stability?
Shales	Fuel	Deteriorat?
	Diesel?	Aging
	Gasoline?	Storage
	Nitrogen?	Thermal
		Decomp
		Degradat?
		Derived

(a) A coal term was added later.

TABLE 3

Literature Citations for Each Descriptor or Key Word Level

Key Words	A. Shale or Shales	A plus Fuel Term (B)	A Plus B plus Descriptor C
Chem. Abstracts	4,169	463	49
NTIS	1,323	324	43

<u>2.3.1 Review of Current Knowledge with Respect to Trace Impurities and Fuel Stability</u>

<u>2.3.1.1 Nitrogen Compounds in Petroleum Derived Fuels</u> -- A number of studies have been made of the nitrogen content of petroleum fractions boiling near the middle distillate (i.e., diesel) fuel range.[2-5] The nitrogen content of petroleum fuels rises sharply with boiling point in the upper portion of the distillate fuel boiling range. Thus, wide range fuels have higher nitrogen levels. The strongly basic pyridine and quinoline nitrogen compounds have been found in both unprocessed material (i.e., crude oil virgin cuts) and fuel range cuts produced via catalytic cracking. Anilines, which are strongly basic, have only been reported in catalytically cracked products and have not been reported in crude oil. The major classes of nitrogen compounds are pyrroles, indoles, carbazoles, quinolines and pyridines, all of which have been reported in both crude oils and cracked products. A number of studies of the distribution of nitrogen compounds between basic and non-basic types have been made. Richter et.al.[6] indicate that, in a study of 14 widely different crude oils, the ratio of basic to total nitrogen varies only between 0.25 to 0.34. Thus, all types of nitrogen species are present in petroleum. However, the <u>total</u> nitrogen level in petroleum-derived crudes is quite low and no nitrogen level specifications currently exist.

The situation is quite different with respect to synthetic crudes, especially those derived from oil shale. In such liquids, the total nitrogen content can be as high as 3%.[1,7] In addition, it has been estimated that 61% of the molecules in shale liquids may contain at least one heteroatom, nearly 40% of which are nitrogen.[8] The

heterocyclic nitrogen in these synthetic crudes is incorporated in five-
or six-membered rings, most of which are unsaturated. These can be
either basic or nonbasic. Pyridines and saturated heterocyclic ring
compounds (indoline, hexahydrocarbazole) are generally basic, while
pyrroles tend to be nonbasic. The small quantities of nonheterocyclic
nitrogen compounds present in liquid fuels include anilines, aliphatic
amines, and nitriles.

Such nitrogen compounds are especially difficult to remove.
A number of investigators have reported that catalytic removal of nitro-
gen compounds from both petroleum and shale oil fractions is much more
difficult than sulfur removal.[9,10] It is extremely important, there-
fore, to determine which nitrogen compounds will be deleterious to
quality in synthetic fuels, which types can be tolerated and at what
levels.

2.3.1.2. Stability Consideration in Petroleum Based Fuels --
The term "fuel stability" is defined as the resistance of a fuel to
change.[11] This can refer to "storage" stability under ambient condi-
tions or "thermal" stability which is resistance to degradation under
high temperature stress. Such change or degradation in fuels manifests
itself in a variety of ways including:

- Development of Color
- Sediment Formation
- Change in Physical Properties
- Change in Chemical Properties (or Fuel Composition)
- Change in Combustion Properties.

Of these, the first three are most conveniently measured and are commonly
used to assess fuel degradation.

The stability of various petroleum products has been extensively studied since the 1920's. A number of reviews are available of which those by White,[11] Nixon[12], Hogin and Clinkenbeard,[13] Ward and Schwartz[14], Rosenwald[15] and Medley and Cooley[16] are specially recommended.

Briefly, these findings indicated that fuel stability depends on fuel composition, refining processes and storage conditions. With respect to hydrocarbon composition, stability decreases in the order: paraffins, naphthenes, aromatics, olefins, and diolefins.[11] This is, in general, the order of susceptibility to autooxidative attack and polymerization reactions which are thought to be the major cause of gum or sediment formation. In addition to hydrocarbon types, a variety of trace impurities in the fuel significantly influence fuel stability. Most important of these are thiols, di and polysulfides, certain reactive oxygen containing compounds and some nitrogen compounds, especially pyrroles.

An excellent study on the mechanism of gum formation in gasolines during simulated storage conditions was carried out by Morrell and co-workers.[17-19] Peroxides could be detected early in the gasoline storage period when no aldehyde, acid, or gum was present. The rate of peroxide formation accelerated with time. Aldehydes begin to appear later in the reaction and their concentration increased more gradually than peroxides. Acid formation began still later in the reaction. Gum deposits appeared when rather large amounts of hydroperoxides were formed but before any large amounts of aldehydes or acids. A plot of gum content vs. time was similar to a plot of ROOH vs. time. This suggests that aldehydes and acids are products of secondary reactions,

not gum precursors.[20] Induction periods were often observed.[20] In a study of the gum formed in gasoline it was found that, in addition to C, H and O, N and S were also present in substantial quantities in the sediment.[21] It thus appears that gum is formed at least partially by cooxidation reactions of reactive hydrocarbon and thiols or pyrroles.[19,21] Thiols may also exert an influence by oxidizing to sulfonic acids which can then catalyze the condensation of pyrroles.[11] At any rate, removal of many sulfur compounds leads to improved storage stability of most petroleum products.[19] Other impurities, such as metals can catalyze hydrocarbon autooxidation but their influence is complex.

Taylor has extended these results in thermal stability studies.[22,24] He established the importance of dissolved oxygen content in promoting deposit formation in fuels of the JP-5 type.[22,23] By reducing the O_2 level from 70 ppm to 1 ppm he was able to increase the breakpoint temperature of some fuels from 287°C (550°F) to as high as 593°C (1100°F). However, some fuels did not respond well to this treatment. Taylor found that such fuels contained trace impurities, especially sulfur or oxygen containing compounds that in themselves promoted deposit formation. [23,24] Thus, a truly "high stability" fuel must be relatively free of both O_2 and such trace impurities.

2.3.1.3 Role of Nitrogen Compounds in Fuel Instability -- It has been known for a long time that nitrogen compounds can contribute to fuel instability in petroleum derived fuels.[11,12,25] However, because of the low level of nitrogen in most crude oils, the problem was not considered serious in most instances. As pointed out above, however, the high nitrogen content in shale liquids and the relative difficulty of

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removing it has prompted a renewed interest in the effect of nitrogen compounds in recent years.

The relationship between total nitrogen and thermal stability is illustrated in Figure 2, where three jet fuels, prepared by catalytic hydrotreating shale liquids, were subjected to the standard JFTOT thermal stability test.[26] Clearly, the higher the nitrogen content of a fuel, the poorer its thermal stability. Some of the samples shown in Figure 2 were severely hydrotreated yet still retained significant amounts of nitrogen and exhibited poor thermal stability.[26]

Certain nitrogen compounds are also known to have adverse effects on color stability of various petroleum distillates.[27-32] Nixon has discussed the effects of trace impurities on storage stability of jet fuels derived from petroleum.[12] He states that pyrrolic compounds and some sulfur containing species are quite deleterious to fuel stability while most amines are not harmful. The most unstable fuels appear to be those high in both pyrrolic nitrogen and olefinic hydrocarbons.[11,12]

Oswald and Noel[27] found that pyrroles reacted with O_2 or peroxides in hydrocarbon solvents to form polymeric sediments of a type called "pyrrole black". A tentative formula (Structure I) was proposed:

I

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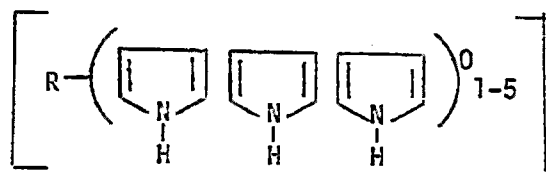
FIGURE 2

Variation of JFTOT Breakpoint
Temperature with Nitrogen Level after Hydrotreatment
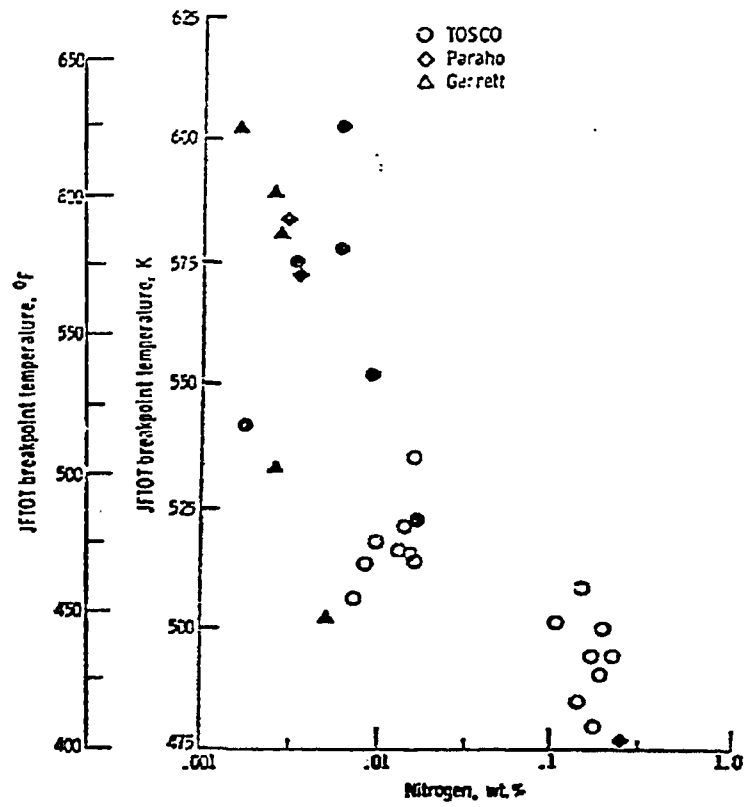
Source: Reference 26, plus Exxon Data (solid symbols).

The actual mechanism for sediment formation, however, is not well understood nor has its importance in fuel instability been fully appreciated. Some workers have observed that deposits are promoted by acids[29-32] and both olefins and thiols have been implicated as participating in sediment formation under certain conditions.[27-32]

Recent work by Frankenfeld and Taylor has shown that nitrogen compounds promote sediment or sludge formation in JP-5 jet fuel stored under ambient conditions.[33] The reaction was first noted by an almost immediate darkening of the fuel. This was followed by the appearance of sludge which continued to increase on standing. These experiments clearly establish the importance of nitrogen compounds in sediment formation. The reactions to form such sludge were strongly influenced by acids, light and oxygen present in the fuel.[33]

These observations led to a more extensive study of the effects of nitrogen compounds on sediment formation.[34,35] The effects of a variety of different nitrogen compounds as well as other trace impurities and storage conditions were investigated using purified n-decane as a model fuel.

It was found that not all nitrogen compounds are deleterious to fuel stability. This is illustrated by screening data presented in Table 4.

TABLE 4

Effects of 2,000 ppm of N Compounds on
Sediment Formation in n-Decane (Stored in Light)

Compound Type	Sediment (g/500 g Decane) After 60 Days Storage
Pyrrole	0.4
Alkyl Pyrroles	0.2-2.0
Indole	0.05
Alkyl Indoles	0.05-2.0
Carbazole	.005
Aryl Amines	0-.005
Alkyl Amines and Amides	0

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The compounds giving the most sediment were all of the pyrrole and indole type. None of the amines or amides studied produced sediment although considerable darkening of the fuel was observed with some of the amines. It appears that the most deleterious compounds fall into the weak to non-basic classification. Basic nitrogen compounds are much less important in promoting sediment formation. The various pyrroles and indoles also vary among themselves with respect to sediment formation. Those with alkyl groups in positions 2 and 5 are especially reactive. In fact, the structural elements identified for greatest reactivity were:

- At least one double bond.

- An alkyl group at position 2 or 5.

- An unsubstituted carbon at position 3 or 4.

Other findings from this recent work include the following:[34,35]

- Light is a strong catalyst for sediment formation. Model fuels containing 2,5-dimethylpyrrole (DMP) stored in UV or sunlight produced sediment as much as ten times faster than dark stored samples. However, the difference was greater early in the storage period. Simply storing fuels in the dark is not sufficient to prevent the sediment from forming.

- Dissolved oxygen also plays a role. Deoxygenated fuels afforded about 1/5 the amount of sediment after 15 days in the light and 1/10 under dark storage. This ratio fell to 1/2 and 1/4 respectively after 60 days. A combination of exclusion of light and deoxygenation reduced sediment by 87% over 60 days and by over 95% over 15 or 30 days in preliminary tests.

- Organic acids accelerate sediment formation with DMP while phenols have the opposite affect. The phenols studied varied considerably in their ability to retard sediment formation. The most effective found so far has been di-t-butylphenol.

- The effects of sulfur compounds on nitrogeneous sediment formation was variable. Sulfides and alkyl mercaptans had little or no influence. Aromatic thiols inhibited

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sediment formation early in the storage period but actually accelerated the reaction later.

● Moisture and mineral acids have only minor effects.

Frankenfeld and Taylor also investigated the structure of the sediments obtained in order to better understand the reaction process. Infrared and mass spectral methods were used as well as determination of the elemental composition of the sediments.[34,35] The material consisted mainly of partly oxidized trimers and tetramers of the parent nitrogen compound.

2.3.1.4 Nitrogen Compounds and Color Stability in Hydrocarbon Fuels -- Several recent reports have appeared linking nitrogen compounds with color formation in hydrocarbon fuels.[36-39] Kajikawa and Kawaguchi observed that color development in petroleum derived kerosene was enhanced by the presence of nitrogen compounds, especially of the pyrrole, quinoline, and alkylpyridine type.[37,38] Kerosene which had nitrogen compounds carefully removed was much more color stable. This report is in good agreement with the work of Frankenfeld and Taylor[39] who observed that many nitrogen compounds contributed to color formation in model systems whether sediment was formed or not. Recently these same workers have observed[36] that hydrotreating actual shale liquids which are black and opaque can afford a nearly colorless product. This may well be due to the removal of nitrogenous color bodies during hydrotreating.[36] It is, of course, still unknown to what extend the development of color can contribute to operating difficulties in fuels.

2.3.1.5 Studies with Actual Shale Liquids -- Frankenfeld and Taylor[40] exposed a sample of hydrotreated Paraho shale oil JP-5[41] to sunlight and collected the sediment which formed. Although still only

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partly characterizea, it shows some resemblance to the sediment obtained from 2,5-dimethylpyrrole.[42] Brinkman, Whisman and Bowden[43] subjected a number of fuels, including some derived from shale liquids to accelerated storage tests. The infrared spectra of the sediment collected is also similar to that reported by Frankenfeld and Taylor.[34]

Brinkman, Whisman and Bowden[43] also reported the gum contents of the various fuels after various storage periods at 43.3°C (110°F). Thirteen weeks under these conditions are considered equivalent to one year's storage at ambient temperatures.[11] These gum levels varied considerably. Although the highest gum was obtained from a high nitrogen shale liquid there was no _direct_ relationship between nitrogen content and gum formation. The thermal stability of all the synthetic fuels was poor as measured by the JFTOT test.[43]

Solash, Nowack and Delfosse evaluated a JP-5 type fuel derived from shale.[44] Although this material performed well in engine tests, it produced excessive NO_x emissions, showed poor thermal stability and had a freeze point and viscosity value that did not meet specifications. Considerable gum was also encountered when the fuel was first received but the fuel was improved significantly in this regard by redistillation. Other methods of treatment such as clay percolation, acid treatment and urea extraction helped improve most of the poor properties of the fuel but a 30% loss in original volume was estimated if a specification fuel were to be obtained.

Hazlett, Hall and Burnett studied the aging of crude shale oil at 50°C for eight weeks.[45] They estimated this was equivalent to about one year's storage under ambient conditions. They observed increases in viscosity and the total amount of high molecular weight material but concluded that such changes were minimal.

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Dinneen and Bickel studied gum formation in shale oil naphtha.[46] They obtained considerable amounts of tar, especially in aerated samples. These workers concluded that basic nitrogen compounds, such as pyridines, contribute significantly to gum formation. Mapstone, however, found that purified tar bases did not add to gum formation while non-basic pyrroles did.[47] Davydov, et.al.[48] claim that tar bases actually conferred enhanced thermal stability on fuels while Englin, et.al.[49] reached the opposite conclusion.

It appears from the foregoing discussion that nitrogen compounds play a definite but, as yet, poorly defined role in fuel stability. Many seeming discrepancies exist, some of which are due to different evaluation techniques. Much additional work is needed before the nitrogen question can be thoroughly understood. A major objective of the work was to make a contribution toward clearing up some of these unanswered points.

2.3.1.6 Nitrogen Compounds in Shale Liquids -- The composition of shale liquids, especially with respect to nitrogen has been studied by a number of investigators.[50-52] (See also Appendix I.) In a preliminary study of shale oil light distillates Poulson reported the breakdown shown in Table 5. The major compound classes he identified were pyridines, quinolines, pyrroles and indoles.[50] Dinneen[52] investigated the various classes separately and identified nearly every possible methyl- and ethyl-substituted pyrrole and several nitriles. Cook[52] identified a variety of anilines in shale liquids and also obtained evidence for heterocyclic compounds containing more than one nitrogen atom per molecule. Multi-nitrogen compounds have also been identified in petroleum.[53] These included azacarbazoles, azapyridines, azaindoles and various imidazoles. Similar

TABLE 5

Predominant Classes of Nitrogen Compounds in a Shale Oil Light Distillate[50]

Nitrogen Type	Wt.% of Total Nitrogen
Alkylpyridines	42
Alkylquinolines	21
Alkylpyrroles (N-H)	8
Alkylindoles (N-H)	7
Cyclic amides (pyridones, quinolines)	3
Anilides	2
Unclassified very weak bases (N-alkylpyrroles and N-alkylindoles?)	4
Other unclassified very weak bases (reduced to non-titratable types and not sulfoxides)	3
Non-Basic (nontitratable) nitrogen in original light distillate	8
Analytical loss	2
TOTAL	100

types are likely to be found in shale liquid as well. This program will concentrate on compounds of the type described in this section.

2.3.1.7 Nitrogen Levels and Specific Nitrogen Compounds in Coal and Coal Liquids -- Coal liquids appear to have slightly less nitrogen, on the average than the shale but significantly more than petroleum.[1,54-57] Hauck reports that most coals contain 1-2% N with bituminous coal slightly higher in nitrogen than peat or lignite.[54] Wolk, et.al.[55] found that the nitrogen levels in a number of coals varied over a rather narrow range from 1.0-1.6%. The properties of the coals they studied are shown in Table 6. Lanning, et.al.[57] report similar results, with nitrogen values on whole coals ranging from 0.6-1.6%.

Analyses for some coal liquids produced by mild hydrotreating as reported by Lanning[57] are shown in Table 7. Nitrogen levels ranged from 0.43-1.45 wt.% in crude liquids to much lower levels in liquids which had "upgraded" by more severe hydrotreating. As expected sulfur

TABLE 6

Properties of Some Raw Coals

	Bituminous					Subbituminous			
	Kentucky		Illinois #6	Pittsburgh		Middle Kittaning	Kalparowitz	Big Horn	Wyodak
	#4	#9,11 12,13		#8	#8				
Proximate Analysis									
Wt.%									
Ash	8.4	17.2	11.7	8.3	8.3	9.7	6.3	4.4	7.3
Volatile Matter	39.2	37.8	42.0	34.1	42.8	40.3	43.9	42.5	46.4
Fixed Carbon	52.3	45.0	46.4	57.6	48.9	50.0	49.8	53.1	46.3
Ultimate Analysis									
Wt.%									
Hydrogen	5.1	4.8	4.8	5.1	5.1	5.3	5.1	4.6	4.8
Carbon	73.0	60.7	70.2	76.8	73.9	72.8	72.5	69.4	66.0
Nitrogen	1.3	1.2	1.4	1.6	1.2	1.3	1.0	1.2	1.1
Oxygen	9.0	11.3	9.3	6.7	7.5	7.5	14.7	19.9	20.4
Sulfur	3.1	5.5	3.2	1.5	4.0	3.1	0.4	0.5	0.4
Ash	8.5	16.5	11.1	8.3	8.3	10.0	6.3	4.4	7.3
Forms of Sulfur									
Wt.%									
Sulfate	0.26	0.47			0.00	0.01	0.02		
Pyritic	1.42	3.08		.66	2.1	1.32	0.00	.14	
Organic	1.35	1.95		.83	1.9	1.77	0.38	.40	

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TABLE 7

Properties of Crude and Upgraded Coal Liquids

Coal	Pittsburgh	Illinois #6 (A)	Illinois #6 (B)	W.Ky.	Colstrip	Wyodak		Lignite
				CRUDE LIQUIDS				
Nitrogen, Wt. %	0.44	1.45	1.10	1.28	0.64	0.48	---	0.43
Oxygen, Wt. %	.59	---	1.34	2.09	1.61	1.08	---	1.55
Sulfur, Wt. %	<.01	0.17	<0.01	0.02	<0.01	<0.01	---	<0.01
				UPGRADED LIQUIDS		(A)	(B)[a]	
Spec. gr., 60/60°F	0.993	1.006	0.992	0.989	0.987	0.955	0.922	0.983
SSU vis. @ 100°F	441	129	126	89	263	96	56	181
SSU vis. @ 130°F	189	65	86	---	123	---	---	123
Pour point, °F	+5	<+5	<+5	<+5	+20	+70	+65	+45
Carbon, Wt. %	89.2	90.1	88.6	88.2	88.1	88.9	88.0	89.0
Hydrogen, Wt. %	10.8	9.9	10.3	10.7	10.6	11.0	11.9	10.8
Sulfur, Wt. %	<0.01	0.03	0.02	0.02	<0.01	<0.01	<0.01	<0.01
Nitrogen, Wt. %	.20	.444	.250	.287	.192	.095	.008	.250
Oxygen, Wt. %	.28	.50	.19	.32	.34	.17	.04	.61
Distillation, Wt. %								
<200°C	10.0	12.3	11.4	16.6	11.5	13.9	18.3	12.3
200°-325°C	21.7	27.3	27.9	26.1	21.5	26.7	30.3	24.0
325°-425°C	20.3	20.7	22.5	22.8	21.1	21.3	19.1	20.7
425°-540°C[b]	26.6	19.1	23.7	19.7	20.9	25.2	25.3	21.0
>540°C[b]	16.2	6.4	7.5	9.3	18.4	11.2	6.3	15.0
Asphaltenes, Wt. %	4.7	14.3	6.8	5.2	6.6	1.2	0.1	6.7

(a) Upgraded on same temperature-time program as Illinois No. 6(B).

(b) Asphaltenes removed from >425°C residuum.

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levels are more easily reduced than nitrogen. Interestingly, Lanning, et.al. found that, upon distillation of "upgraded" liquids the nitrogen contents increased with increasing final boiling point. In shale liquids the distribution of nitrogen has been reported as much less sensitive to boiling range.[35,59-60]

Previous work on coal structure[1] suggests that most organic nitrogen compounds found in coal will be of the aniline, indole, quinoline and carbazole type. In general, this is true[61] although the situation is more complex. This is illustrated by the partial list of compound types reported in Table 8. Nevertheless, the range of nitrogen compound types in coal liquids appears more limited than in shale.[61]

TABLE 8

Nitrogen Compounds in Coal and Coal Liquids

	Reference[a]
Acridine	61,62,66
Carbazole	54,61,62,72
Methyl carbazole	61
Pyridines and anilines	61,63,64,65
phenyl pyridines	61,72
trimethyl pyridine	63
ethyl pyridine	63
Quinolines and isoquinolines	61,62,6365
dimethyl- or ethylquinoline	61
benzoquinolines	61
tetrahydroquinolines	61,72
Indole	72
Fatty amines	63
Purines	63
Porphyrins	63

[a] References appear in Section 4.

2.3.1.8 Stability Studies of Coal Liquids -- The storage
and thermal stability of coal liquids has not been so extensively studied
as shale. Early reports on the stability of coal tars[67-71] indicates
they can degrade rapidly, especially in the presence of air. Increases
in viscosity, loss in volatility and sludge are often observed.[67,72]
Phenolic compounds have been implicated in the formation of condensation
products.[70]

Even less has been reported on the stability of refined liquids
derived from coal. Reynolds included some coal-derived fuels of the JP-5
type in his thermal stability studies.[26] All the coal liquids he studied,
however, had been severely hydroprocessed and were quite low in nitrogen.
As a result no correlation between nitrogen level and thermal stability
was found. However, a possible positive correlation of breakpoint tempera-
ture with hydrogen content was reported. In general, coal and shale
derived fuels with comparable nitrogen and hydrogen contents showed
similar stability characteristics. Shale liquids with high nitrogen
contents, on the other hand, were much less stable.[26] Brinkman,
Whisman and Bowden investigated both the thermal and storage stability
of a coal liquid as well as that of shale liquids.[43] The coal liquid failed
to meet both the visual rating requirements and the pressure drop limit
of the JFTOT test. In storage stability tests at 110°F, the coal liquid
showed little gum formation initially. However, by 32 weeks moderate
to high gum levels were observed.[43] Nowack[66] submitted four
samples of JP-5 type fuel derived from coal to 26 weeks storage at 110°F.
All fuels showed some increase in gum formation over this period. How-
ever, only one sample was judged excessive in this regard. It is,
perhaps, noteworthy that the gum formation in the four fuels was roughly

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proportionate to their nitrogen content. Nowack recommends the use of an oxidation inhibitor to retard gum formation in coal-derived fuels.[66]

2.4 RESULTS OF ACCELERATED STORAGE TESTS USING SINGLE, PURE COMPOUNDS

2.4.1 Improvements in Accelerated Storage Test Procedures

A change in accelerated storage test procedures has resulted in significantly better precision among replicate samples. Previously[78] samples were transferred, hot, from drying oven to desiccators and allowed to cool before weighing. Current procedure calls for turning off the heat after 1-1/2 hours and allowing both oven and samples to return to ambient temperatures in vacuum. Reproducibility of data using the old procedure is shown in Table 9. The average standard error for No. 2 diesel experiments is 50% for the data shown. That for JP-8 was much better, 12%, since JP-8, a lower boiling, more highly refined fuel, is easier to remove completely. One potential cause for error was incomplete evaporation of the No. 2 diesel. The new procedure is designed to improve this. Results with the new technique are shown in Table 10. The average standard error for these experiments is 10%, a significant improvement over previous experience. Some additional examples of typical replicate data are given in Table 13 and Table 23 (Section 2.7). A complete description of the test is given in Section 2.2.3.

2.4.2 Results of Accelerated Storage Tests with Various Nitrogen Compounds

Two sets of experiments were carried out. The first, using various pyrroles and indoles was designed mainly to extend earlier model systems work[34,35] to actual broad range fuels and to select a base fuel for the current program; considerable additional information was, however, obtained. The second set was aimed at expanding the current knowledge to additional, as yet, untested, nitrogen compounds. The tests were conducted by adding

TABLE 9

Reproducibility of Sediment Data Using Old Technique[a]

Fuel	Replicate	DMP[b] (ppm)	Storage[c] Days	Deposits (mg/100 cc)			
				Total[d]	Mean $\bar{x}$	Standard Deviation δ	Standard Error $\delta/\bar{x}$ x 100
Diesel	1	1500	14	96.6	217.3	170.7	79%
	2			338.0			
	1	750	14	38.8	74.5	50.5	68%
	2			110.2			
	1	1500	28	452.1	572.9	170.8	30%
	2			693.6			
	1	750	28	358.1	431.8	104.2	24%
	2			505.5			
Average: $\delta/\bar{x}$							50%
JP-8	1	1500	14	123.1	114.8	11.7	10%
	2			106.5			
	1	750	14	36.3	60.2	33.8	56%
	2			84.1			
	1	1500	28	341.5	343.0	2.1	0.60%
	2			344.4			
	1	750	28	133.0	133.5	.64	0.47%
	2			133.9			
	1	1500	56	566.5	575.9	13.3	2.3%
	2			585.3			
	1	750	56	259.1	254.2	6.91	2.7%
	2			249.3			
Average: $\delta/\bar{x}$							12%

(a) 120°C 1-1/2 hour -- cool in desiccator.
(b) DMP = 2,5-dimethylpyrrole; ppm level given as nitrogen basis.
(c) All at 43.3°C (110°F).
(d) Not adjusted for fuel blank.

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TABLE 10

Reproducibility in Diesel Fuel Using New Drying Technique[a]

Replicate	N-Cpd (ppm N)[b]	Storage (Days)	(°F)	Deposits (mg/100 cc)			
				Total	Mean, $\bar{x}$	Standard Deviation δ	Standard Error $\delta/\bar{x} \times 100$
1	DMP (1500)	14	72	33.9	28.1	8.20	29%
2				22.3			
1	DMP (1500)	14	110	189.0	188.6	0.64	0.34%
2				188.1			
1	DMP (1500)	14	150	342.7	343.7	1.34	0.39%
2				344.6			
1	DMP (750)	28	72	42.1	43.8	2.40	5.5%
2				45.5			
1	DMP (750)	24	110	126.3	101.8	34.7	34%
2				77.2			
1	DMP (1500)	28	72	110.0	108.5	2.12	2.0%
2				107.0			
1	DMP (1500)	28	150	647.2	627.8	27.4	4.4%
2				608.4			
1	DMP (150)	28	110	41.5	50.0	12.0	24%
2	3-MeI (1350)			58.5			
1	DMP	28	110	239.9	246.3	8.98	3.6%
2				252.6			
1	DMP (150)	28	110	57.9	57.7	0.35	0.61%
2	Isoq (1350)			57.4			

Average: $\delta/\bar{x}$ 10%

(a) 120 C for 1-1/2 hours followed by vacuum pump overnight.
(b) = 2,5-dimethylpyrrole, 3 - MeI = 3-methylindole, isoq = isoquinoline.

various amounts of purified model compounds to the base fuels. The resulting mixtures were stored in the dark at 110°F or 150°F for the specified time periods then analyzed for color and sediment as described in Section 2.2.3.

2.4.2.1 Color and Sediment Formation with Pyrroles and Indoles in Various Base Fuels -- The results of ASTM D1500 color tests for various compounds of this type in both No. 2 diesel and JP-8 fuels for up to 56-day periods are given in Table 11. The color development was usually significantly greater in the diesel than the jet fuel; the only exception being 3-methylindole. The pyrroles, especially 2,5-dimethylpyrrole (DMP), 1,2,5-trimethylpyrrole and 2,5-dimethyl, 3-ethylpyrrole developed color very rapidly. DMP reached an ASTM color level of 4 in 14 days, near the maximum value for this program. Colors rated at 4 are black to red-black and almost opaque. The color for 2,5-dimethyl-3-ethylpyrrole was too dark to measure by 14 days.

The quantities of insoluble, adherent and total sediment for various pyrroles and indoles for storage periods (in the dark at 110°F) of 14, 28, and 56 days are given in Table 12. The results shown are the average of 2-10 replicates. These are continually being refined as more data are obtained. Three different diluents were used, pure n-decane, JP-8 and No. 2 diesel. Typical replicate results from some 7-day runs are given in Table 13. These were made for comparisons needed for the interaction studies described in Section 2.5.

It is clear that the nature of the diluent has a significant effect on sediment formation with the quantities increasing as the model fuel becomes more complex (broader boiling range) and less pure. This is much more marked with 2,5-dimethylpyrrole (DMP) but is also noticeable

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TABLE 11

Color Tests for Pyrroles and Indoles Stored in Jet Fuel and No. 2-Diesel at 110°F

Replicate	Nitrogen Compounds	PPM Added[a]	ASTM D1500 Color							
			No. 2 Diesel				JP-8			
			Start	14 Days	28 Days	56 Days	Start	14 Days	28 Days	56 Days
1	None	---	0.5	0.5	0.5	0.5	0.0	0.0	0.5	0.5
2	None	---	0.5	0.5	0.5	0.5	0.0	0.0	0.0	0.5
1	DMP[b]	1500	0.5	3.5	4.0	(e)	0.0	3.0	3.5	2.5
2	DMP[b]	1500	0.5	4.0	4.0		0.0	3.0	3.5	2.5
1	DMP[b]	750	0.5	3.0	3.5		0.0	2.0	2.0	2.0
2	DMP[b]	750	0.5	3.0	3.0		0.0	2.0	2.5	2.0
1	DMP[b]	150	0.5	2.0	2.0		0.0	1.5	1.5	1.5
2	DMP[b]	150	0.5	1.5	1.5		0.0	1.0	2.0	1.5
1	2-Methylindole	1500	0.5	0.5	1.0		0.0	0.5	1.5	1.0
2	2-Methylindole	1500	0.5	0.5	1.0		0.0	0.5	1.5	1.0
1	2-Methylindole	750	0.5	0.5	1.0		0.0	0.5	1.5	0.5
2	2-Methylindole	750	0.5	0.5	1.0		0.0	0.5	1.0	1.5
1	2-Methylindole	150	0.5	0.5	0.5		0.0	0.5	1.0	1.0
2	2-Methylindole	150	0.5	0.5	0.5		0.0	0.5	1.0	2.0
1	3-Methylindole	1500	0.5	0.5	1.0		0.0	1.0	3.0	3.0
2	3-Methylindole	1500	0.5	0.5	1.0		0.0	1.0	2.5	3.0
1	3-Methylindole	750	0.5	0.5	0.5		0.0	0.5	2.0	2.5
2	3-Methylindole	750	0.5	0.5	1.0		0.0	0.5	2.0	2.0
1	3-Methylindole	150	0.5	0.5	0.5		0.0	0.5	0.5	1.5
2	3-Methylindole	150	0.5	0.5	0.5		0.0	0.5	0.5	1.0
1	Indole	1500	0.5	0.5	0.5	0.5	NT[c]			
2	Indole	1500	0.5	0.5	0.5	0.5				

TABLE 11 (Cont'd.)

| | | | ASTM D-1500 Color | | | | | | | |
| Replicate | Nitrogen Compounds | PPM Added[a] | No. 2 Diesel | | | | JP-8 | | | |
			Start	14 Days	28 Days	56 Days	Start	14 Days	28 Days	56 Days
1	Pyrrole	1500	0.5	0.5	0.5	0.5	NT[c]			
2	Pyrrole	1500	0.5	0.5	0.5	0.5				
1	1,2,5-trimethylpyrrole	1500	0.5	2.0	---	---	NT[c]			
2	1,2,5-trimethylpyrrole	1500	0.5	2.0	---	---				
1	1,2,5-trimethylpyrrole	150	0.5	2.0	---	---	NT[c]			
2	1,2,5-trimethylpyrrole	150	0.5	2.0	---	---				
1	1,2,5-trimethylpyrrole	1500	0.5	2.5	2.5	---	NT[c]			
2	1,2,5-trimethylpyrrole	1500	0.5	2.5	2.5	---				
1	1-methylpyrrole	1500	0.5	0.5	0.5	0.5	NT[c]			
2	1-methylpyrrole	1500	0.5	0.5	0.5	0.5				
1	1-phenylpyrrole	1500	0.5	0.5	0.5	0.5	NT[c]			
2	1-phenylpyrrole	1500	0.5	0.5	0.5	0.5				
1	2,4-dimethyl-3-ethyl pyrrole	1500	0.5	(d)	(d)	(d)				
2	2,4-dimethyl-3-ethyl pyrrole	1500	0.5	(d)	(d)	(d)				

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(a) Nitrogen basis.
(b) DMP = 2,5-dimethypyrrole
(c) NT = not tested in JP-8
(d) Too dark to measure
(e) Colors with DMP are generally too dark to measure by 56 days.

TABLE 12

Sediment from Fuels Containing Pyrroles and Indoles After Storage at 110°F

Nitrogen Compounds	Level (ppm)[a]	Sediment (mg/100cc)[b]								
		14 Days			28 Days			56 Days		
		Insol	Adherent	Total	Insol	Adherent	Total	Insol	Inherent	Total
Normal Decane[c]										
2,5-Dimethylpyrrole	750	35.0	9.1	44.1	28.3	73.7	102.0	---	---	---
JP-8										
2,5-Dimethylpyrrole	1500	19.6	88.9	108.5	11.1	302.6	313.7	138.1	448.2	586.3
	750	7.3	54.0	61.3	6.6	133.9	140.5	5.4	248.3	253.7
	150	0	0.8	0.8	.5	17.8	18.3	3.6	37.6	41.2
2-Methylindole	1500	trace	trace	trace	1.9	12.7	14.6	0.5	25.4	25.9
	750	0.4	0	0.4	3.6	7.8	11.4	2.5	12.4	14.9
	150	trace	trace	trace	trace	trace	trace	trace	0.5	0.5
3-Methylindole	1500	1.0	3.0	4.0	0.9	.10	1.0	0.3	trace	0.3
	750	1.1	trace	1.1	0.8	.10	0.9	0.2	0.7	0.9
	150	0	0	0	.09	.10	1.0	0.5	0.1	0.6
No. 2 Diesel										
2,5-Dimethylpyrrole	1500	51.6	165.9	217.5	123.4	373.3	496.7	559.6	236.1	795.8
	750	60.1	28.4	88.5	65.3	180.5	245.8	216.0	164.1	380.1
	150	17.6	6.2	23.8	31.9	9.0	40.9	17.9	43.4	61.3
2-Methylindole	1500	trace	trace	trace	1.1	11.9	13.0	1.0	25.4	26.4
	750	0	0.4	0.4	2.8	7.0	9.8	2.5	12.5	15.0
	150	4.5	15.5	20.0	5.0	trace	5.0	0.2	3.0	3.2
3-Methylindole	1500	3.0	0	3.0	0.1	0.5	0.5	0.5	4.0	4.5
	750	0.2	0	0.2	0.1	0.1	0.2	0.9	0.8	1.7
	150	0	0	0	0.1	0.1	0.2	0.4	0.7	1.1

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TABLE 12 (Cont'd.)

No. 2 Diesel (Cont'd.)

Sediment (mg/100cc)[b]

Nitrogen Compounds	Level (ppm)[a]	14 Days			28 Days			56 Days		
		Insol	Adherent	Total	Insol	Adherent	Total	Insol	Adherent	Total
Pyrrole	1500	0	0.7	0.7	3.0	trace	3.0	0.5	trace	0.5
Indole	1500	0	trace	trace	0.4	1.0	1.4	trace	1.0	1.0
1-Methyl pyrrole	1500	0	0	0	0	0	0	0	0	0
1-Phenyl pyrrole	1500	0	0	0	0	0	0	0	0	0
2,4-Dimethyl-3-ethyl pyrrole	1500	14.5	5.3	19.8	10.3	16.0	26.3	---	---	---
1,2,5-trimethylpyrrole	1500	67.8	19.8	82.6	---	---	---	474.0	352.0	826.0
	750				92.3	24.8	117.1			
	150	14.4	5.8	20.2	24.0	4.3	28.3	9.1	25.1	34.6

(a) Nitrogen basis.
(b) Average of 2-10 replicates, diesels corrected for blank; blank corrections: 14-day 0; 28-day 0.5, 56-day 0.5.
(c) Purified over silica gel and activated alumina.[34,35]

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TABLE 13

Typical Replicate Results with 2,5-Dimethyl
Pyrrole Stored in No. 2 Diesel Fuel at 110°F (7 Days)

Replicate	DMP (ppm)	Sediment (mg/100 ml) after 7 Days		
		Insol	Adherent	Total
1	750	23.9	0.7	24.6
2	"	23.2	2.0	25.2
3	"	25.5	---	25.5
4	"	23.6	1.1	24.7
5	"	21.3	0.1	21.4
6	"	23.5	0.1	23.6
7	"	25.7	0.4	26.1
8	"	26.0	0.3	26.3
Mean ($\overline{x}$)		24.1	0.6	24.7
Standard Deviation				1.53

with some indoles, especially 3-methylindole. The reason for these differences is not yet known. It may be due to differences in the hydrocarbon content of the fuels (basically solvent effects) or, more likely, to the presence of trace impurities which promote sediment formation. Such impurities would be more prevalent in the more complex fuels.

Although either No. 2 diesel or JP-8 could be used as the diluent for additional work, it was decided to concentrate on the former for this year's work, since diesel fuel is more in line with DOE's long range plans. For certain experiments, for example the pure hydrocarbon studies described in Section 2.6 where a more highly refined diluent was required, JP-8 was employed as well as the diesel. It is anticipated that future work will require all three model fuels. However, emphasis will be placed on the diesel and JP-8 as well as some actual shale liquids. Additional studies are indicated in order to understand this "broad range fuel effect" better.

A plot of sediment formation vs. time for DMP stored in JP-8 at 110°F is given in Figure 3 and for No. 2 diesel in Figure 4. The range of replicates for each point is shown to indicate the spread in the data. Good reproducibility is especially true for storage in JP-8. These plots show a generally linear response, consistent with earlier observations with DMP under dark storage conditions.[34,35,39] Light storage affords quite different curves.[34,35,39]

A plot of sediment formation as a function of DMP concentration in JP-8 (expressed as ppm N) is shown in Figure 5. Again linear curves are obtained. Although a rigorous kinetic analysis cannot be made with current data, these plots suggest that sediment formation with DMP in JP-8 may be first order in DMP.

FIGURE 3

Sediment Formation from 2,5-DMP in JP-8 Stored at 110°F
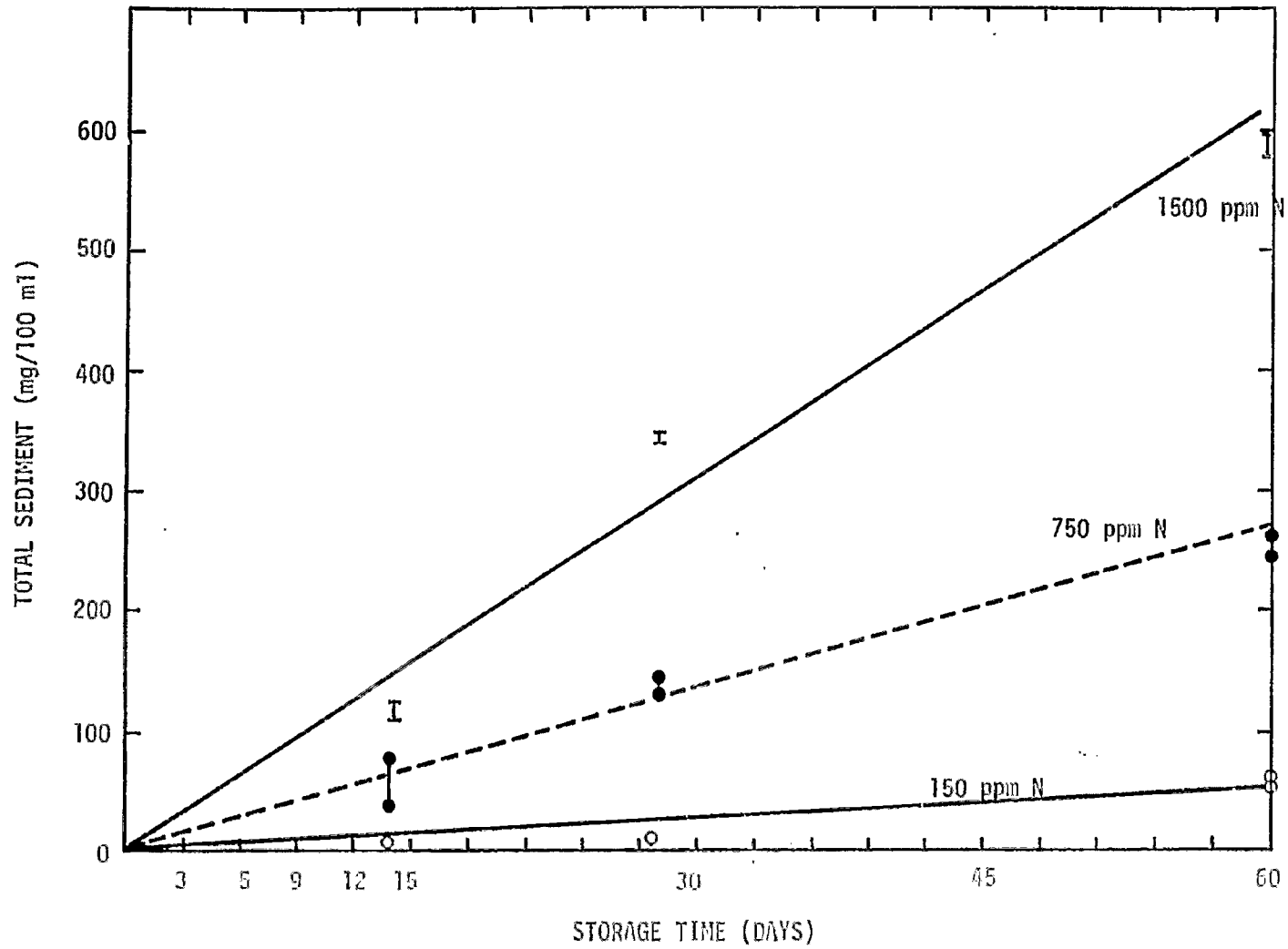
FIGURE 4

Sediment Formation with 2,5-DMP in No. 2 Diesel Stored at 110°F
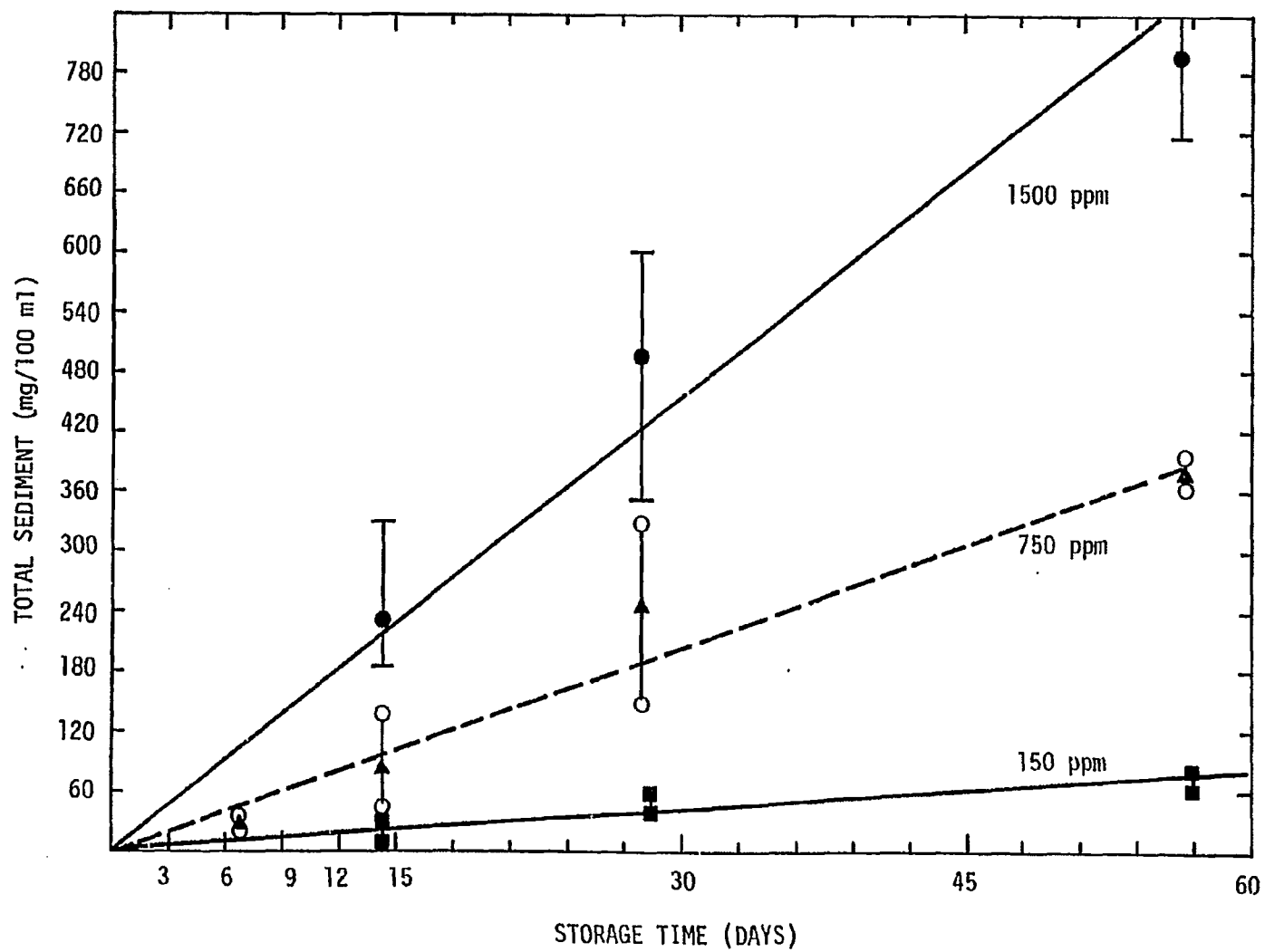
FIGURE 5

Effect of Concentration on Sediment Formation with 2,5-DMP in JP-8 at 110°F

38
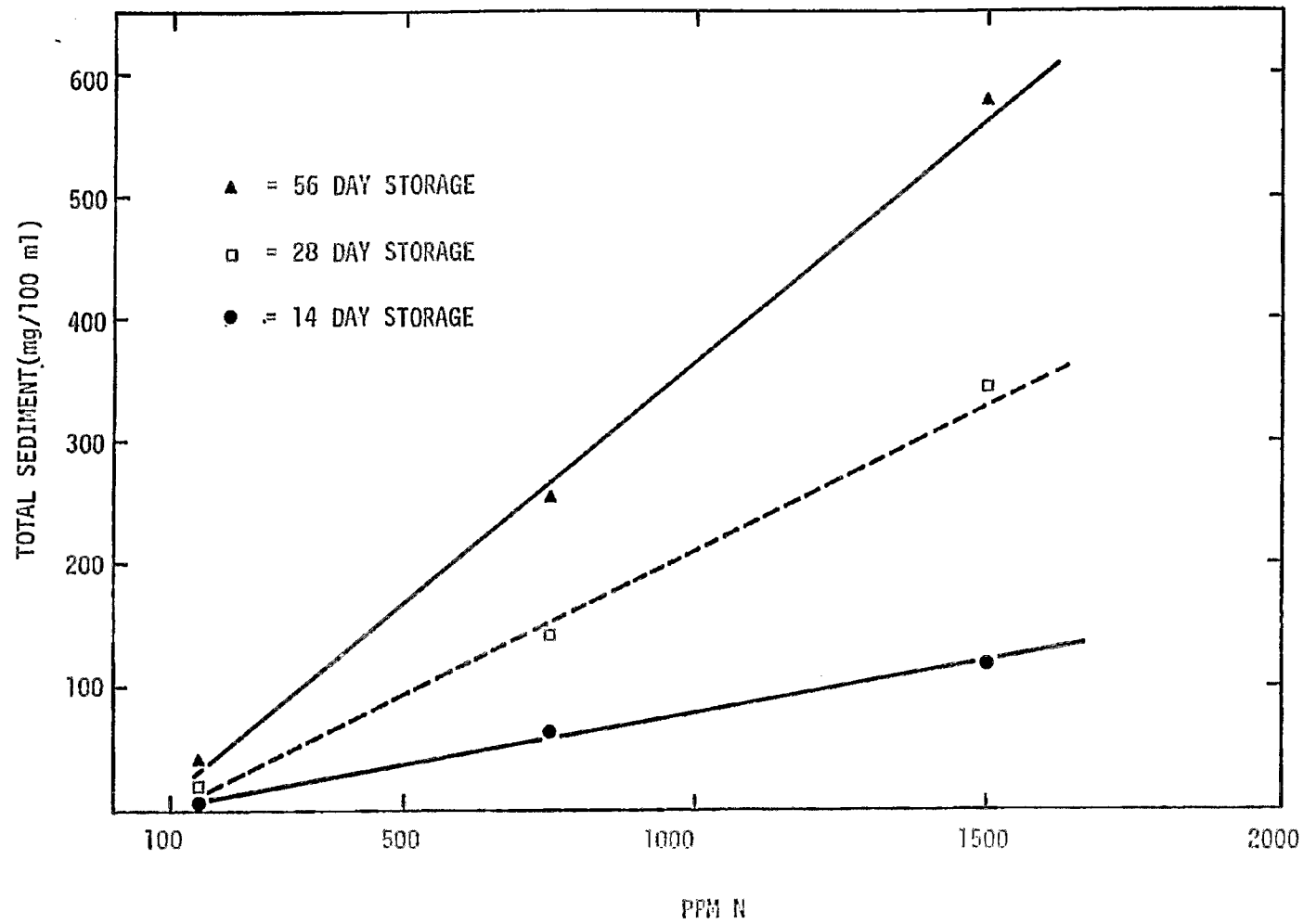
2.4.3 Effects of Other Nitrogen Compounds on Sediment Formation in No. 2 Diesel Fuel

The compounds employed and their structures are given in Figure 6. Pyrroles and indoles are included for comparison. These compounds were chosen since (1) they are representative of nitrogen compounds found in coal and shale liquids,[34] (2) they are readily available; (3) they provide opportunities for correlations between structures and activity. Color tests through 56 days storage at 110 F are given in Table 14. Only 7-azaindole, 3-methylpyridazine and quinaldine showed significant color formation.

The insoluble, adherent and total sediments produced by these compounds through 56 day storage are shown in Table 15. These sediments tended to be more tacky and "adherent" than those obtained from pyrroles and indoles. All were quite dark in color. The compounds, 7-azaindole, 2-methylpiperazine, 2-methylpyrazine and quinaldine all produced measurable sediment in 28 and 56 days.

2.4.4 Effects of Structure on Tendency Toward Sediment Formation

The results of studies on structural effects which have been carried out so far are summarized in Figure 7. Here the nitrogen compounds are grouped as "strongly deleterious", "moderately deleterious" and "relatively harmless" with regard to their relative tendencies to form sludge in hydrocarbon fuels. The differences between groupings, especially between strongly and moderately deleterious is quite large. These limited data seem to indicate that, with few exceptions, the deleterious compounds are those which contain <u>heterocyclic nitrogens with an alkyl group adjacent to nitrogen</u>. In addition, the few compounds studied with <u>more than one</u> alkyl group appear to be much more prone to sediment formation than the mono alkyl homologs. Finally, as observed previously[34,35] the 2,5-dimethyl configuration appears significantly more reactive than 2,4 (compare 1,2,5-

39

FIGURE 6

Structures of Nitrogen
Compounds Used in Stability Studies
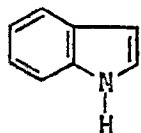
INDOLE
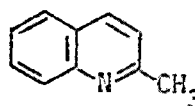
QUINALDINE
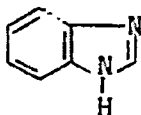
BENZIMIDAZOLE
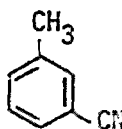
m-TOLYLNITRILE
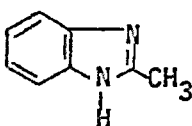
2-METHYLBENZIMIDAZOLE
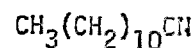
$CH_3(CH_2)_{10}CN$ n-UNDECYLCYANIDE
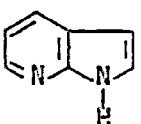
7-AZAINDOLE
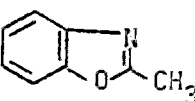
2-METHYLBENZOXAZOLE
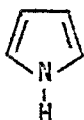
PYRROLE
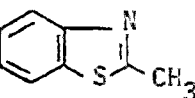
2-METHYLBENZOTHIAZOLE
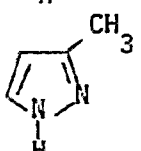
3-METHYLPYRAZOLE
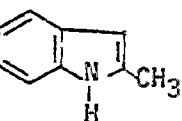
2-METHYLINDOLE
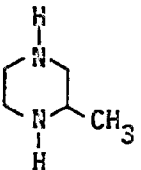
2-METHYLPIPERAZINE
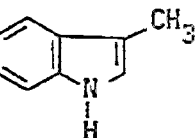
3-METHYLINDOLE
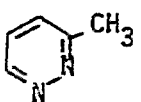
3-METHYLPYRIDAZINE
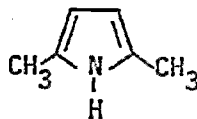
2,5-DIMETHYLPYRROLE
(DMP)
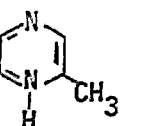
2-METHYLPYRAZINE
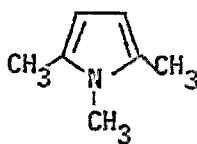
1,2,5-TRIMETHYLPYRROLE

2,4-DIMETHYL-3-ETHYLPYRROLE

40
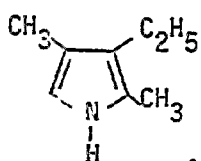
TABLE 14

ASTM Color Test Results for Various Nitrogen Compounds Stored in No. 2 Diesel Fuel at 100°F

Replicate	Nitrogen Compound[a]	ASTM D1500 Color			
		Start	14 Days	28 Days	56 Days
1	None	0.5	0.5	0.5	0.5
2	None	0.5	0.5	0.5	0.5
1	Benzimidazole[b]	---	---	---	---
2	Benzimidazole[b]	---	---	---	---
1	7-Azaindole	0.5	0.5	0.5	1.5
2	7-Azaindole	0.5	0.5	0.5	1.5
1	3-Methylpyrazole	0.5	0.5	0.5	0.5
2	3-Methylpyrazole	0.5	0.5	0.5	1.0
1	2-Methylpiperazine	0.5	0.5	0.5	0.5
2	2-Methylpiperazine	0.5	0.5	1.0	0.5
1	3-Methylpyridazine	0.5	1.0	1.0	1.0
2	3-Methylpyridazine	0.5	1.0	1.0	1.0
1	2-Methylpyrazine	0.5	0.5	0.5	0.5
2	2-Methylpyrazine	0.5	0.5	0.5	0.5
1	Quinaldine[c]	0.5	0.5	1.0	2.5
2	Quinaldine[c]	0.5	0.5	1.0	2.0
1	m-Tolylnitrile	0.5	0.5	0.5	0.5
2	m-Tolylnitrile	0.5	0.5	0.5	0.5
1	n-Undecylcyanide	0.5	0.5	0.5	0.5
2	n-Undecylcyanide	0.5	0.5	0.5	0.5
1	2-Methylbenzoxazole	0.5	0.5	1.0	0.5
2	2-Methylbenzoxazole	0.5	0.5	1.0	0.5
1	2-Methylbenzothiazole	0.5	0.5	1.0	0.5
2	2-Methylbenzothiazole	0.5	1.0	1.0	0.5

(a) All added at 1500 ppm N; see Figure 6 for structures.
(b) Insoluble in No. 2 diesel.
(c) Quinaldine = 2-methylquinoline.

TABLE 15

Effects of Various Nitrogen Compounds
on Sediment Formation in No. 2 Diesel Fuel Stored at 110°F

Nitrogen Compound[b]	Sediment (mg/100°C)[a]								
	14 Days			28 Days			56 Days		
	Insoluble	Adherent	Total	Insoluble	Adherent	Total	Insoluble	Adherent	Total
Benzimidazole	(c)	---	---	---	---	---	---	---	---
7-Azaindole	0	0.7	0.7	0	0.3	0.3	0	8.7	8.7
3-Methylpyrazole	0	0.4	0.4	trace	trace	trace	0	0.7	0.7
2-Methylpiperazine	0.4	0.5	0.9	0.3	3.3	3.9	0	6.9	6.9
3-Methylpyridazine	0	1.9	1.9	0	4.2	4.2	0	4.0	4.0
2-Methylpyrazine	0.7	0.2	0.9	0	0.8	0.8	0	1.1	1.1
Quinaldine[d]	0.4	trace	0.4	0	1.8	1.8	0.1	4.7	4.7
m-Tolylnitrile	trace	trace	trace	0	0.6	0.6	trace	trace	trace
n-Undecylcyanide	0.5	trace	0.5	0	0.2	0.2	trace	trace	trace
2-Methylbenzoxazole	0.5	0.3	0.8	0	0.6	0.6	trace	trace	trace
2-Methylthiazole	0.5	trace	0.5	0	0.4	0.4	trace	trace	trace

(a) Average of two replicates; blank values subtracted; corrections: 14 days - 0; 2 Days - 0.5; 56 days - 0.5
(b) All added at 1,000 ppm N, see Figure 6 for structures.
(c) Insoluble in No. 2 diesel.
(d) Quinaldine = 2-methylquinoline

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FIGURE 7

Structural Effects on Sediment Formation

Strongly Deleterious >> Moderately Deleterious > Relatively Harmless
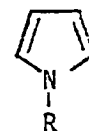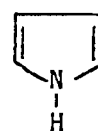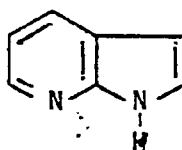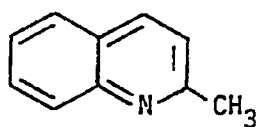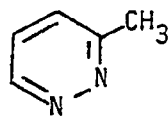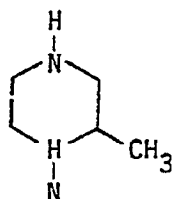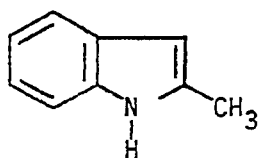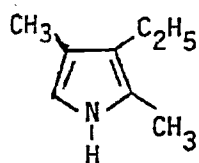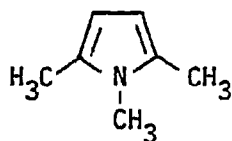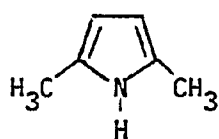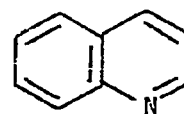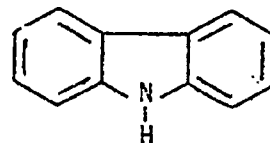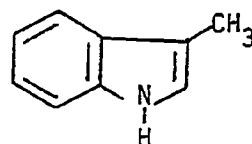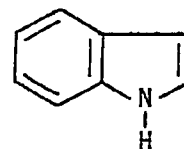
RNH₂, ArNH₂, RCONH₂,
RCN, ArCN

trimethyl pyrrole with 2,4-dimethyl, 3-ethylpyrrole in Table 12, (Section 2.4.2.1). These observations are based on limited data and must be regarded as tentative. However, they do support previous suggestions[34,35,39] that sediment from pyrrolic compounds arises from oligomerization through the adjacent methyl groups (see Figure 8). The partial structures shown in Figure 8 are supported by elemental, infrared and mass spectral analyses[34,35] and provide a possible explanation for the need for alkyl groups adjacent to nitrogen for large scale sediment formation. Additional work with other model compounds is indicated in order to confirm these findings.

FIGURE 8

Possible Partial Structures for DMP Sediment[5]

I

II

III

IV
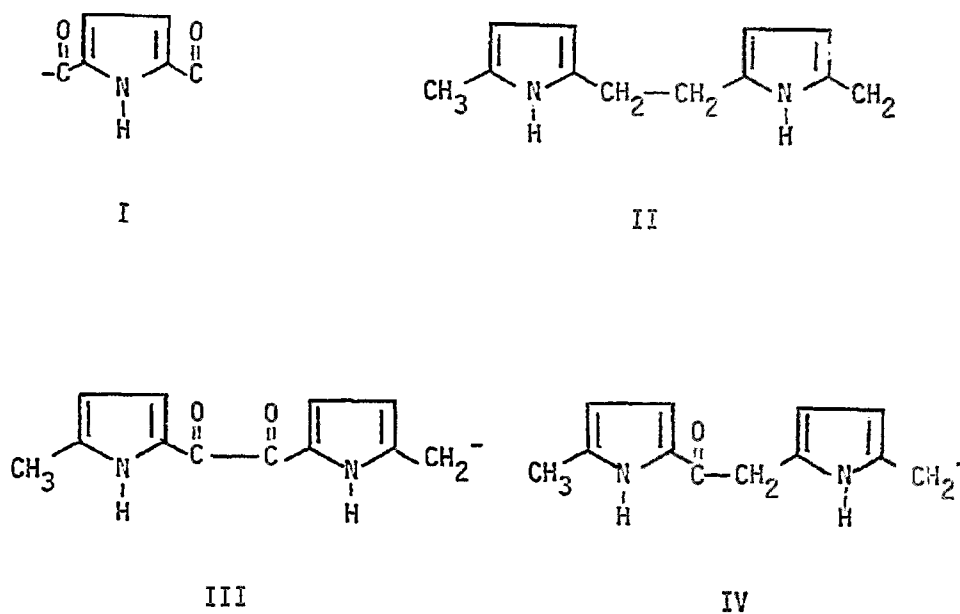
2.4.5 Studies with Sulfur and Oxygen Compounds in No. 2 Diesel

A variety of sulfur and oxygen compounds are known to be present in shale and coal liquids. The most prevalent compound types discovered to date are given in Table 16. Representatives of these classes are currently under investigation to determine whether they can either form sediment themselves or interact with nitrogen compounds to either enhance or retard sediment formation by the nitrogen containing species. A few examples of such "positive" and "negative" interactions have been observed previously in both storage[34,35] and thermal[23,24,33] stability studies. These may be quite important and additional work in this area is indicated.

The compounds employed in these studies, that of the effects of sulfur and oxygen compounds alone, are shown in Figure 9. These were selected on the basis of their likely occurrence in shale or coal liquids, and, in certain instances, because they were readily comparable to the analogous nitrogen compounds (e.g., 2,5-dimethylthiophene, 2,5-dimethyl-furan and 2,5-dimethylpyrrole). When tested by themselves (at 3000 ppm S in No. 2 diesel fuel) after 56 days storage at 110°F, no discernible sediment was encountered with any of these compounds except p-toluenesulfonic acid. This materia- afforded large quantities of dark colored tar after 56 days although only trace amounts were visit.e at 28 days.

2.5 INTERACTIONS BETWEEN PURE COMPOUNDS

Interactions may be quite important to storage stability of synthetic fuels, especially those derived from shale and coal liquids. Previous work[24,33-35] has indicated that certain compounds, which do not produce sediment by themselves, can contribute to or stimulate sediment formation in others ("positive" interaction). In some instances, some materials interact to inhibit sediment formation ("negative" interaction).

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TABLE 16

Oxygen and Sulfur Compounds in Shale and Coal Liquids

Compound Type	References[a]
A. Oxygen Compounds	
Cyclohexanols	73
Isoprenoid ketones, alkyl ketones	51, 73, 74
Tetralones and indanones	73
Alkylphenols	51, 74
Alkoxy phenols	75, 76
Ethers	77
Furans	51, 74
Carboxylic Acids	51, 74
B. Sulfur Compounds	
Alkyl thiols	78, 80
Cyclic Sulfides, Polysulfides	78
Thiophene	51, 78
Alkyl Thiophenes	51, 78
Benzothiophene	51, 78
Disulfides	80

[a]Numbers refer to references in Section 4.

FIGURE 9

Sulfur and Oxygen Compounds Used in Sediment
Formation Studies[a]

p-THIOCRESOL

BENZYLPHENYL
SULFIDE

BENZYLDISULFIDE

THIANAPHTHENE

p-TOLUENESULFONIC
ACID

2,4,6-TRIMETHYLPHENOL

2,6-DI-t-BUTYLPHENOL

$CH_3(CH_2)_{11}SH$ n-DODECANETHIOL

$CH_3(CH_2)_8CO_2H$ n-DECANOIC ACID

DIBENZOFURAN

α-DECALONE

$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_7CH_3$ 2-DECANONE

2,5-DIMETHYL-
THIOPHENE

MENTHOL

2,5-DIMETHYLFURAN

2-NAPHTHALENE-
SULFONIC ACID

THIOPHENOL
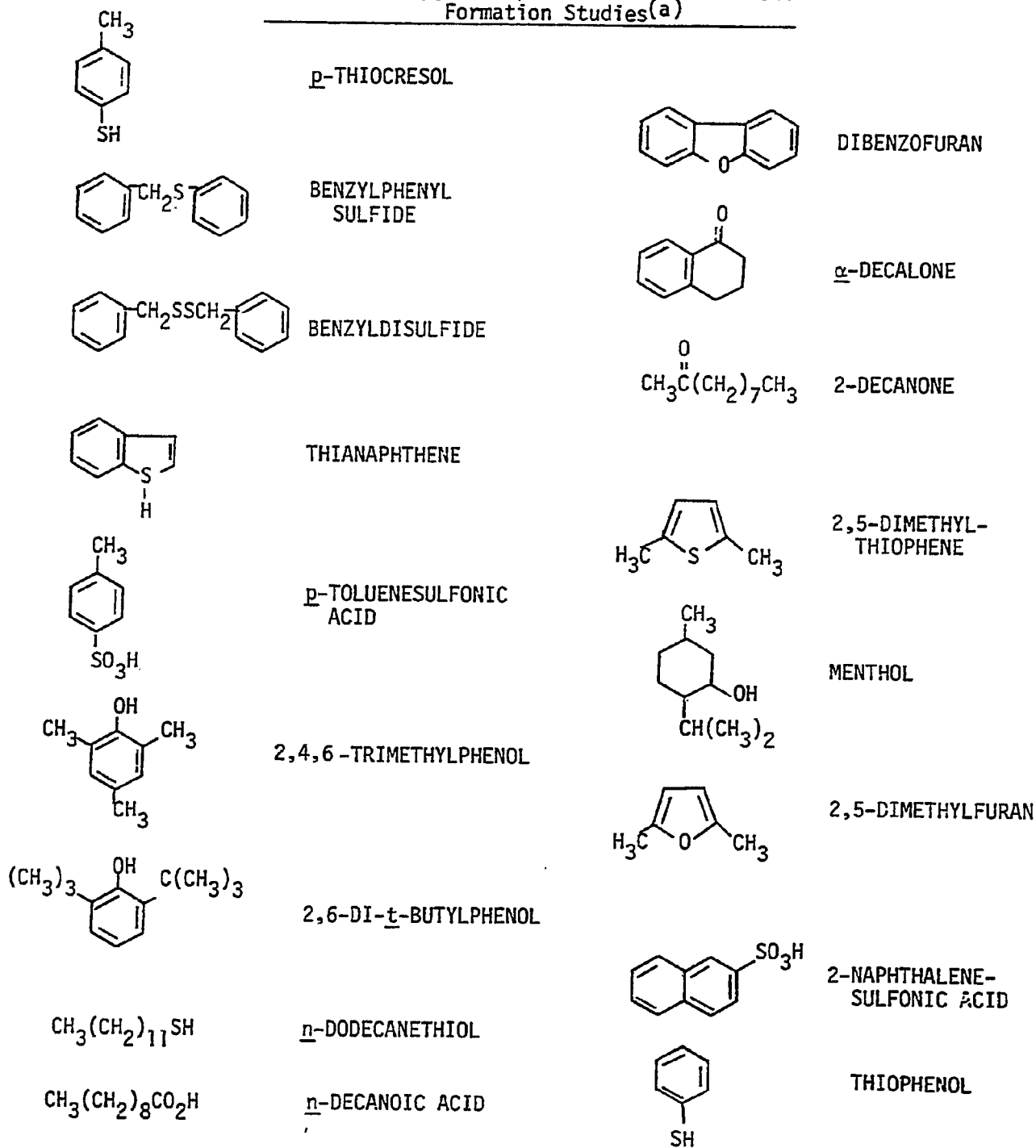
(a) Studies in No. 2 diesel at 110°F.

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These interactions have been demonstrated for thermal stability[58] and, to a very limited extent in the case of storage stability.[34,35] Considerable additional work is needed, however, in this important area. The results of preliminary interaction studies in the present program are summarized in this section.

2.5.1 Interactions Between Pairs of Nitrogen Compounds

The results of a preliminary study to determine whether N-N interactions can occur under conditions of dark storage are given in Table 17. These results are summarized and their significance analyzed in Table 18. In order to determine whether an interaction actually occurred the data were analyzed by means of 2 x 2 factorial experiments. Typical design involving DMP and isoquinoline is shown in Figure 10. The analysis shown in Figure 10 indicates a likely positive interaction after 28 days and clear cut interaction after 56 days. Thus, after 56 days the total sediment obtained with both nitrogen compounds together (127.5 mg/100 cc) was more than double the _sum_ of the two which would be expected if they acted independently (61.8 mg/100 cc). To determine the significance of the results, the data were subjected to Students "t" test.[81] Results are summarized in Table 18. These preliminary results suggest that interactions can occur between DMP and various nitrogen-containing species. These have important implications for fuel stability. Certain compounds, for example, trioctyl amine and isoquinoline, while relatively innocuous when present alone can contribute significantly to sediment formation in the presence of compounds such as DMP. On the other hand, some materials, such as 2-methylindole, may actually have a stabilizing effect. The results of the four tests with 2-methylindole are especially interesting and surprising.

TABLE 17

Nitrogen-Nitrogen Interaction Studies
During 110°F Storage in No. 2 Diesel Fuel

Interaction Exp.	Nitrogen Compounds	Level (ppm N)	Total Sediment[a] (mg/100 cc) after 28 Days	56 Days
(c)	LMP	150	40.9	61.8
(c)	UMP	750	245.8	380.1
(c)	1,2,5-Trimethylpyrrole	150	18.5	---
(c)		750	117.1	---
(c)	3-Methylindole	1500	0.6	4.5
(c)		750	0.2	1.7
(c)	2-Methylindole	1500	13.0	26.4
(c)		750	9.8	15.0
(c)	Isoquinoline	1500	0	0
(c)	Trioctylamine	1500	0	0
1	DMP + 3-Methylindole	150 1350	48.2[d]	94.0[b]
2	DMP + Isoquinoline	150 1350	54.9[d]	127.5[b]
3	DMP + Trioctylamine	150 1350	49.8[d]	115.8[b]
4	DMP + 1,2,5-Trimethylpyrrole	150 150	134.0[b]	--- ---
5	2-Methylindole + 3-Methylindole	750 750	0.2[e]	0.3[e]
6	DMP + 2-Methylindole	150 1350	15.0[d]	27.3[e]

(a) Total of adherent and insoluble sediments.
(b) Average of four replicates.
(c) Not an interaction run-compound tested alone; see Tables 12, 15 (isoquinoline from previous studies).
(d) Average of six replicates.
(e) Average of two replicates.

TABLE 18

Summary of N-N-Interaction Runs[a]

Compound A, ppm	Compound B, ppm	Storage Time (Days)	Type of Interaction[b]	Significance Test[c]
DMP, 150	3-Methylindole, 1350	28	Positive	Doubtful ($t = 1.9$, $p = 0.1$)
DMP, 150	3-Methylindole, 1350	56	Positive	Significant ($t = 5.2$, $.025 > p > .01$)
DMP, 150	Isoquinoline, 1350	28	Positive	Likely ($t = 3.5$, $.05 > p > .025$)
DMP, 150	Isoquinoline, 1350	56	Positive	Significant ($t = 6.3$, $.025 > p > .01$)
DMP, 150	Trioctylamine, 1350	28	Positive	Doubtful ($t = 0.6$, $p = <0.1$)
DMP, 150	Trioctylamine, 1350	56	Positive	Significant ($t = 4.5$, $p = .01$)
DMP, 150	1,2,5-Trimethylpyrrole, 150	28	Positive	Highly significant ($t = 73$, $p = <.005$)
2-Methylindole, 750	3-Methylindole, 750	28	Negative	Highly significant ($t = >100$, $p = <.005$)
2-Methylindole, 750	3-Methylindole, 750	56	Negative	Highly significant ($t = 86$, $p = <.005$)
DMP, 150	2-Methylindole, 1350	28	Negative	Highly significant ($t = 52$, $p = <.005$)
DMP, 150	2-Methylindole, 1350	56	Negative	Significant ($t = 6.5$, $p = .05$)

(a) See Table 17 for details.
(b) "Positive interaction" means combination gave more sediment than sum of two compounds tested alone.
(c) Student's test (see reference 81, section 4).

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FIGURE 10

2 x 2 Factorial Analysis of an Interaction Between
2,5-Dimethylpyrrole (A, 150 ppm) And
Isoquinoline (B, 1350 ppm) in No. 2 Diesel [a]

PRESENCE OF COMPOUND A

	NO	YES
PRESENCE OF COMPOUND B — NO	0.5	40.9 [b]
PRESENCE OF COMPOUND B — YES	0.0 [c]	54.9

28-DAYS STORAGE AT 110°F

PRESENCE OF COMPOUND A

	NO	YES
PRESENCE OF COMPOUND B — NO	0.5	61.3 [b]
PRESENCE OF COMPOUND B — YES	0.0 [c]	127.5

56 DAYS STORAGE AT 110°F

(a) Sediment shows as mg/100 cc.
(b) Amount expected from 150 ppm DMP alone.
(c) Amount from 1350 ppm Isoquinoline alone.

51

They all indicate a statistically significant <u>negative</u> interaction. This needs to be confirmed in future experiments. Typical plots of "positive" N-N interactions are shown in Figure 11. The examples shown are DMP with isoquinoline and trioctylamine.

2.5.2 Interactions Between Nitrogen Compounds and Sulfur or Oxygen Compounds

Previous work suggested that important interactions can occur between nitrogen and sulfur or oxygen compounds.[33-35] Several of these interactions were "negative" (i.e., stabilizing). Several experiments were performed in the present program to test for these interactions in broad range fuels. Results of these are given in Table 19. The interactions discovered and their significance are summarized in Table 20. The thiols, especially the aromatic thiols, gave significant negative interactions with DMP at least up to 28 days storage (see also Figure 12). Such interactions were observed in earlier work, but the effect was reversed on long term storage.[34,35] It has been suggested that this was due to oxidation of the thiols to sulfonic acids; the former being inhibitors and the latter accelerators.[35] Longer term storage tests are planned to investigate this phenomenon.

Surprisingly, no effects were observed with either decanoic acid or 2,6-di-<u>t</u>-butylphenol when tested with DMP in No. 2 diesel fuel. Work in purified decane has indicated a significant accelerating effect with most organic acids including decanoic while phenols are inhibitors.[34,35] This seeming discrepancy was investigated and is described in Section 2.5.3. It would appear that important N-S and, possibly, N-O interactions can occur in broad range fuels. Additional work is indicated and is currently being planned.

FIGURE 11

N-N Interactions

Legend for figure:
- ●—— DMP (150 ppm N) alone.
- ○--- DMP (150 ppm) + Isoquinoline (1350 ppm)
- ■—— DMP (150 ppm) + Trioctylamine (1350 ppm)

(110°F in No. 2 Diesel)

Y-axis: TOTAL SEDIMENT (mg/100 ml)

X-axis: STORAGE TIME (DAYS)
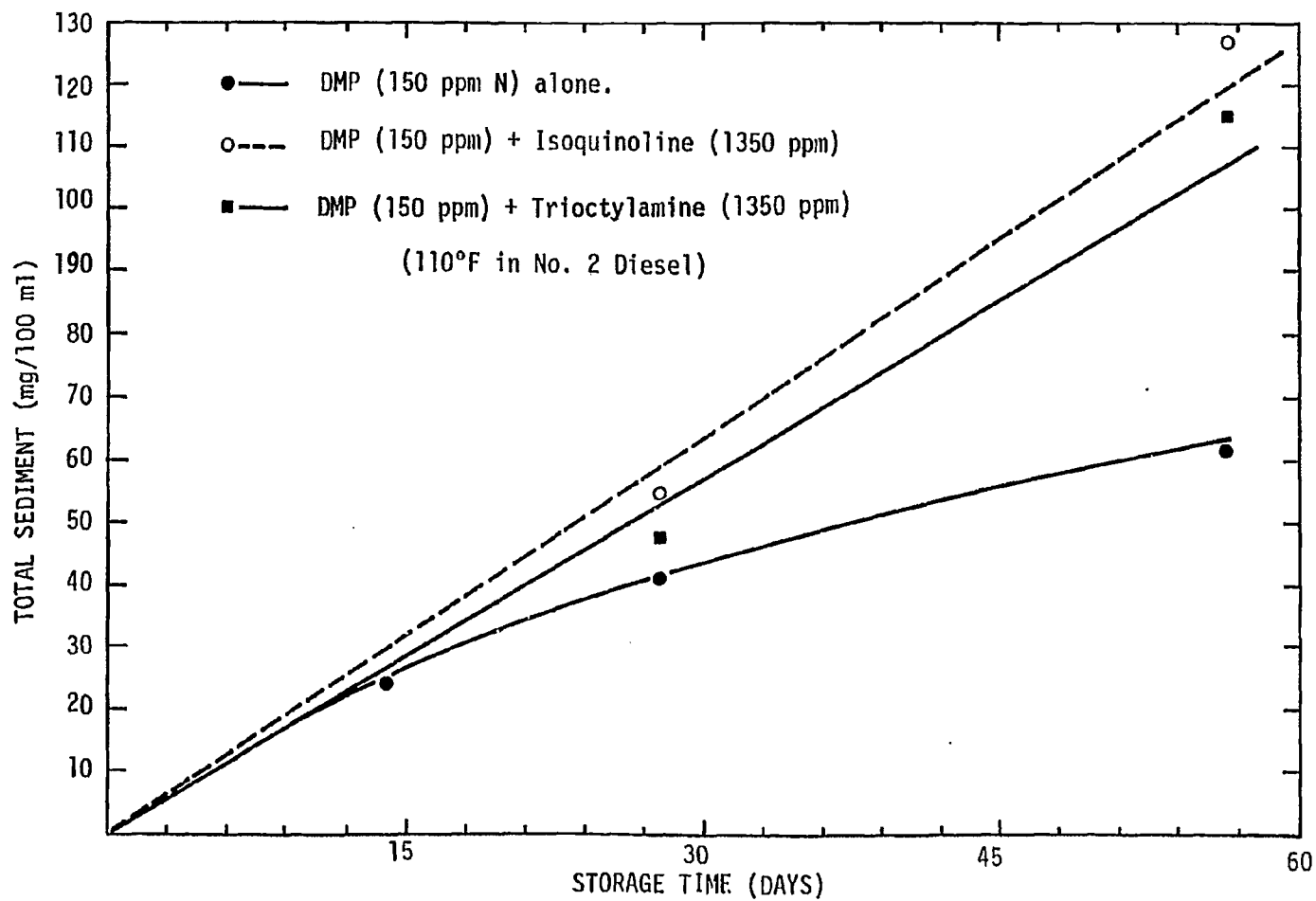
TABLE 19

Interactions Between 2,5-Dimethylpyrrole And Oxygen and Sulfur Compounds in No. 2 Diesel Fuel[a]

Sulfur or Oxygen Compound (ppm)[b]	7 Days Total Sediment[c] (mg/100 cc)	14 Days Total Sediment[c] (mg/100 cc)	28 Days Total Sediment[c] (mg/100 cc)
None	24.7	88.5	245.8
n-Decanoic Acid (100)	----	90.2	256.0
Benzylphenyl Sulfide (3000)	----	95.6	216.1
p-Thiocresol (3000)	12.6	20.3	62.4
Thiophenol (3000)	13.1	14.4	70.7
n-Dodecanethiol (3000)	----	71.6	373.2
2,6-Di-t-butyl phenol (100)	----	107.7	293.5

(a) 2,5-Dimethylpyrrole present at 750 ppm N level in all cases; storage at 110°F in No. 2 Diesel.

(b) S or O basis.

(c) Total of adherent plus insoluble; average of 2 or more replicates.

TABLE 20

Summary of Interactions Between 2,5-Dimethylpyrrole (DMP)
and S and O Compounds in No. 2 Diesel Fuel[a]

Compound A (ppm)[b]	Compound B (ppm)[c]	Storage Time (days)	Type of Interaction[d]	Significance Test[e]
DMP (750)	Decanoic Acid (100)	14	None[f]	
DMP (750)	Decanoic Acid (100)	28	None[f]	
DMP (750)	Benzylphenyl Sulfide (3000)	14	None	
DMP (750)	Benzylphenyl Suflide (3000)	28	None	
DMP (750)	p-Thiocresol (3000)	7	Negative	Significant ($t = 60$; $p = 05$)
DMP (750)	p-Thiocresol (3000)	14	Negative	Highly Significant ($t = 13.0$; $p < .005$)
DMP (750)	p-Thiocresol (3000)	28	Negative	Highly Significant ($t = 19.1$; $p < .005$)
DMP (750)	Thiophenol (3000)	7	Negative	Highly Significant ($t = 11.1$; $p < .005$)
DMP (750)	Thiophenol (3000)	14	Negative	Highly Significant ($t = 71.0$; $p < .005$)
DMP (750)	Thiophenol (3000)	28	Negative	Highly Significant ($t = 28.3$; $p < .005$)
DMP (750)	Dodecanethiol (3000)	14	None	
DMP (750)	Dodecanethiol (3000)	28	Positive	Not Significant
DMP (750	2,6-Di-t-Butylphenol (100)	14	None	
DMP (750)	2,6-Di-t-Butylphenol (100)	28	None	

(a) See Table 19 for experimental details
(b) N Basis.
(c) S or O basis.
(d) "Negative" means combination gave less sediment than sum of components alone.
(e) Reference 81, Section 4.
(f) Positive interactions were observed in other fuel systems (see Section 2.5.3.)

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FIGURE 12

Interactions Between DMP (750 ppm N) and Aromatic Thiols (3000 ppm S)

- ●——— DMP ALONE
- ○——— DMP + p-THIOCRESOL
- ■——— DMP + THIOPHENOL

(110°F IN NO. 2 DIESEL)

TOTAL SEDIMENT (mg/100 ml)

STORAGE TIME (DAYS)
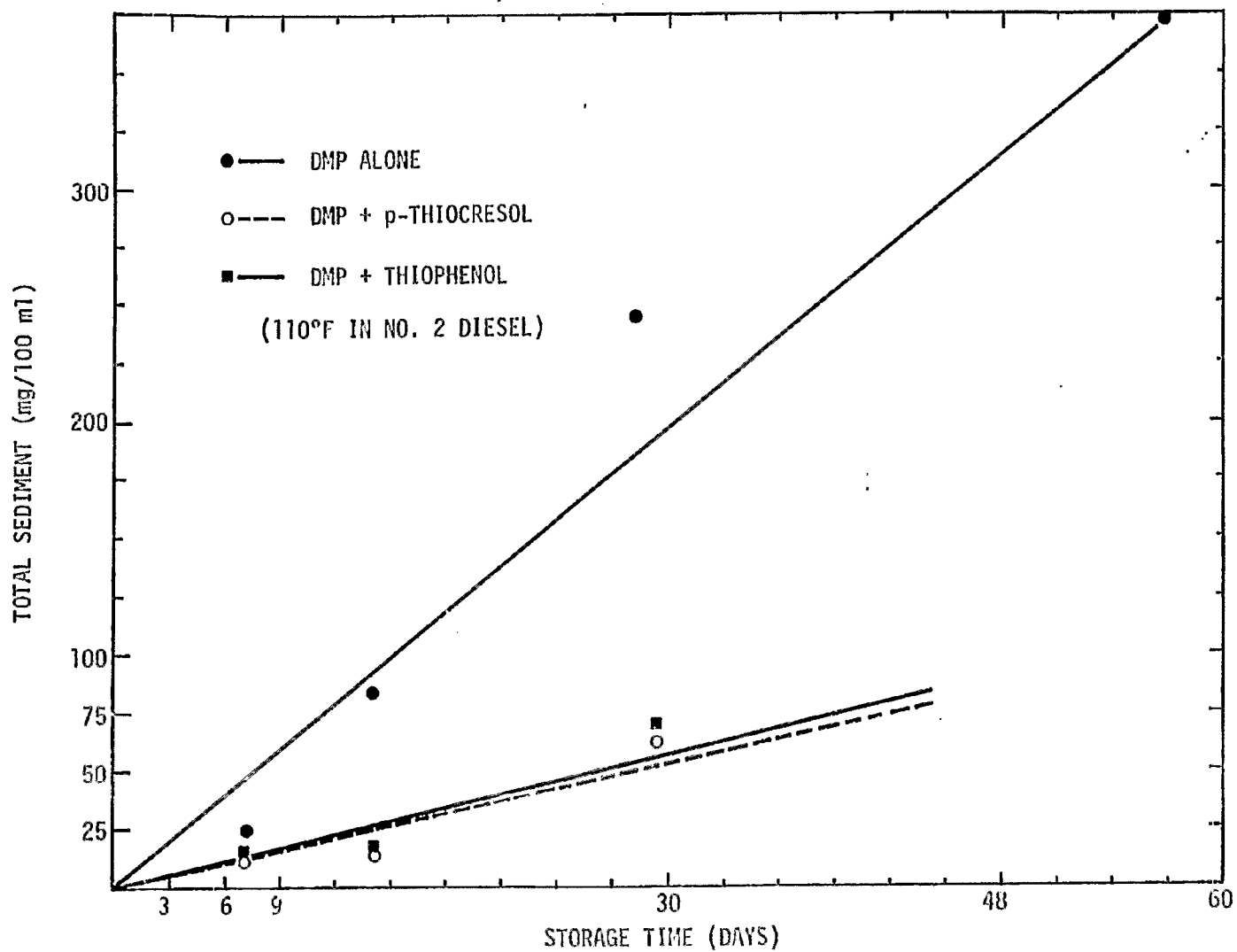
2.5.3 Effects of Decanoic Acid

Experiments using purified n-decane as the diluent at ambient temperatures have shown that organic acids, especially n-decanoic have a strong accelerating effect on sediment formed from DMP.[39,35] The effects were observed in both light and dark storage conditions. Since no interaction could be detected in the present studies (which employed No. 2 diesel as the model fuel under accelerated (110°F) storage conditions) a separate study was undertaken to investigate these seemingly contradictory results. Three diluents, No. 2 diesel, JP-8 and purified n-decane were used and samples were stored both at ambient temperatures and at 110°F. The results are presented in Table 21 and illustrated by the plots in Figure 13. Previous work has shown that decanoic acid alone afforded no sediment or color change in hydrocarbon fuels.[24,34,35]

These results confirmed the previous observation that decanoic acid interacts strongly with DMP in decane to promote sediment formation. A significant positive interaction also exists in JP-8. In diesel, however, no interaction occurs. A possible explanation for these results lies in the fact that the base No. 2 diesel has an appreciable acid titer (Table 1, Section 2.2.1) while both the JP-8 and n-decane were acid free. It is interesting that the curves for DMP in diesel with and without added acid are virtually superimposable with those of both JP-8 and decane with added acid (Figure 13). This suggests that acid, present normally in diesel fuel may contribute to the enhanced sediment formation in that fuel.

2.6 EFFECTS OF HYDROCARBON CONTENT OF BASE FUEL ON SEDIMENT FORMATION

The differences in sediment formation rates observed with various diluents (see Section 2.4.2.1) indicate the chemical characteristics

TABLE 21

Effects of n-Decanoic Acid on Sediment Formation With 2,5-Dimethylpyrrole (DMP) in Various Model Fuel Systems[a]

FUEL	STORAGE Temp (°F)	ppm DMP[c]	ppm R CO$_2$H[d]	Total Sediment[b] (mg/100cc) After 14 Days	28 Days	50 Days
Diesel	72	750	----	18.6	42.6	-----
		750	100	16.1	46.1	-----
	110	750	----	88.5	245.8	380.1
		750	100	88.0	245.0	500.0
JP-8	72	750	----	7.0	-----	-----
		750	100	12.7	-----	-----
	110	750	----	61.3	140.5	253.7
		750	100	84.7	227.0	432.9
n-Decane[e]	RT	750	----	18.3	38.1	-----
		750	100	69.2	103.9	-----
	110	750	----	44.1	101.5	-----
		750	100	92.8	225.2	375.0

(a) Dark storage.

(b) Sum of insoluble and adherent sediments adjusted for blanks (see table 12).

(c) Nitrogen basis.

(d) R CO$_2$H = n-decanoic acid; ppm on oxygen basis.

(e) Purified over silica gel and activated alumina.

FIGURE 13

Effects of Decanoic Acid on Sediment Formation With DMP
(750 ppm) in Various Diluents at 110°F

STORAGE TIME (DAYS)

Legend:
- ○—·—·—· DIESEL PLUS ACID
- ● ———— DIESEL, NO ACID
- ⊕············ JP-8 PLUS ACID
- □ ———— JP-8, NO ACID
- △ —————— DECANE PLUS ACID
- ▲ ———— DECANE, NO ACID

TOTAL SEDIMENT (mg/100 cc)
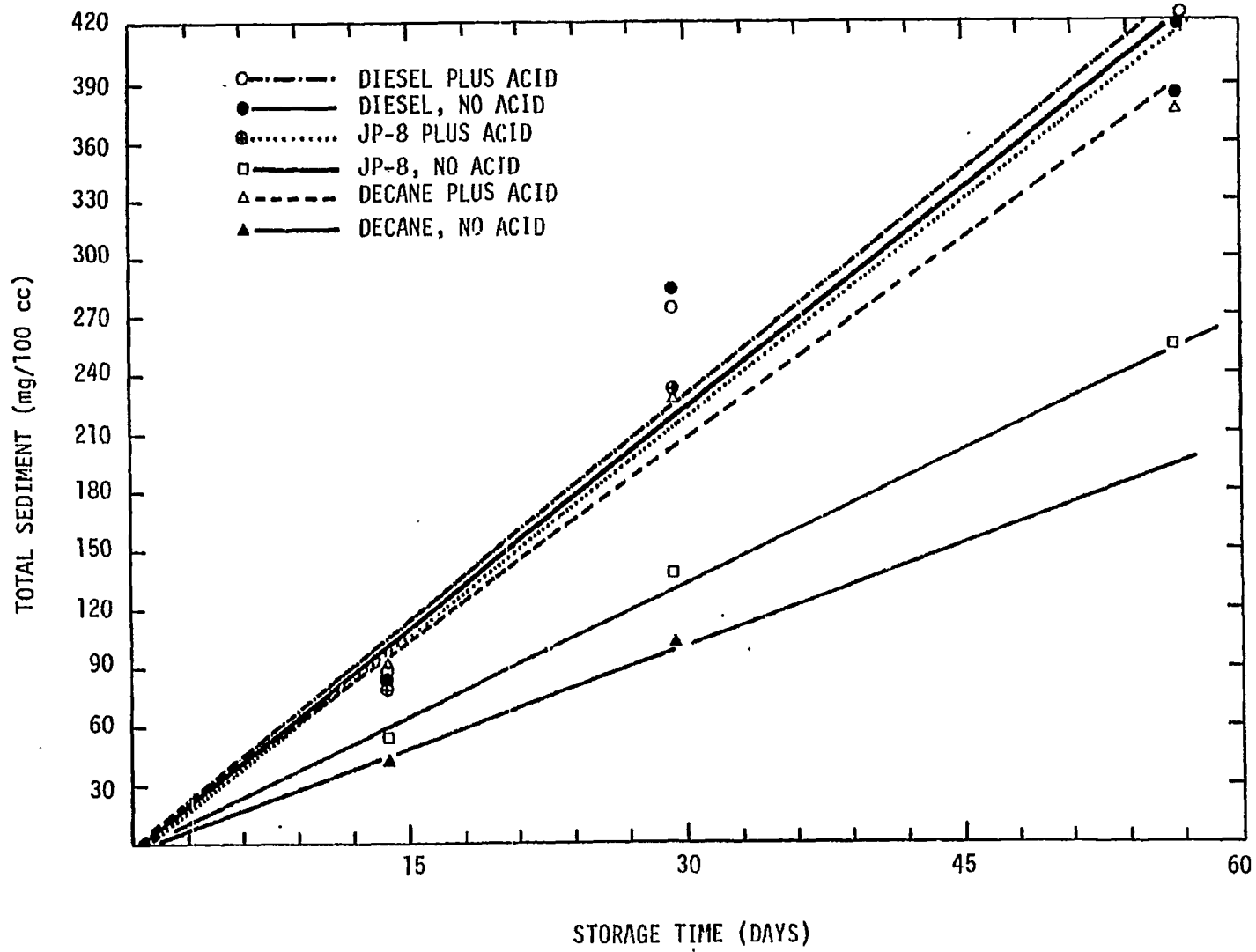
of the base fuels can exert a significant influence on the amounts of
nitrogenous sediment obtained. This may be due to differences in solu-
bility characteristics of the base fuels or to the presence of trace
impurities which accelerate or inhibit sediment formation. The effects
of the hydrocarbon content of the base fuels is currently being studied
with preliminary results reported here. These experiments are carried
out by adding representatives of the most prevalent hydrocarbon types,
n-paraffins, branched paraffins, naphthenes (cycloparaffins) and aromatics
to the base fuels and determining their influence on sediment formation
with various nitrogen compounds. The hydrocarbons are added at levels
approximating their normal occurrence in most distillate fuels.[82] In
addition, certain reactive olefins, known to contribute to gum formation
in petroleum fuels, are being tested. The more highly refined JP-8 is
being used for these experiments because adding small quantities of olefins to a
complex fuel such as No. 2 diesel would likely lead to equivocal results.

Preliminary studies on hydrocarbon effects are summarized in
Table 22. DMP at the 1500 ppm N level was employed as the nitrogen compound.
The data obtained so far indicate only minor effects, if any, due to hydro-
carbon type. However, additional work is required, especially with more
reactive species such as diolefins, and will be carried out in the future.

2.7 EFFECTS OF STORAGE TEMPERATURE-ESTIMATION OF APPARENT ACTIVATION ENERGY

The effects of storage temperature on sediment formation were
studied using DMP as the model compound. Results of 14-day tests with
DMP in both No. 2 diesel and JP-8 are given in Table 23. Arrhenius plots
of the same data are shown in Figures 14 to 15. This permits an estimation

TABLE 22

Effects of Hydrocarbon Types on Sediment Formation With 2,5-Dimethylpyrrole (DMP)-Preliminary Studies(a)

Base Fuel	Hydrocarbon Added	Vol. % Added	Total Sediment (mg/100 ml) After		
			14 Days	28 Days	56 Days
No. 2 Diesel(b)	None	--	217.5	572.8	795.8
	s-Butylbenzene	15	176.1	833.3	--
	Cyclohexane	20	152.0	888.0	--
JP-8	None	--	108.5	313.7	586.3
	s-Butylbenzene	15	93.5	313.2	630.5
	1-Dodecene	5	112.0	311.2	685.5
	α-Methylstyrene	5	118.1	327.8	676.0

(a) DMP Level: 1500 ppm N; storage temp: 110°F.

(b) Average of 2 or more replicates; "total sediment" is sum of insoluble and adherent sediment.

TABLE 23

Temperature Study with 2,5-Dimethylpyrrole (DMP)[a]

Replicate	Fuel	°F	Temperature °C	°K	Total Sediment (mg/100 cc)[b] Repl.	Mean ($\bar{x}$)	St.Dev.(∂)	$\frac{\partial}{\bar{x}}$ (%)
1	Diesel Blank	150°			2.0	1.7	.29	16.9
2					1.5			
3					1.5			
1	Diesel	74	23.3	296.3	42.7	42.9	.92	2.1
2					42.1			
3					43.9			
1	Diesel	115	46.1	319.1	158.3	195.4	35.2	18.0
2					199.8			
3					228.2			
1	Diesel[c]	155	68.3	341.3	373.2	375.4	22.3	6.2
2								
1	JP-8	74	23.3	296.3	20.8	19.7	1.06	5.4
2					19.5			
3					18.7			
1	JP-8	115	46.1	319.1	38.4	135.4	4.88	3.6
2					129.8			
3					138.0			
1	JP-8	155	68.3	341.3	307.0	324.0	15.9	4.9
2					338.4			
3					326.5			

(a) 1500 ppm N; 14-day duration; combined insol. and adherent sediments; 4 replicates unless otherwise stated.
(b) Blank corrections: RT = 0; 115° = 0.5 mg/100 cc; 150° = 1.7 mg/100; No corrections for JP-8.
(c) Two replicates only.

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FIGURE 14

Arrhenius Plot of DMP (1500 ppm N) in No. 2 Diesel
14-Days' Storage (Range of Replicates are Indicated)

155°F

115°F

E_{ACT} = 10.7 Kcal/mole

74°F

TOTAL SEDIMENT (mg/100 cc)

1000/°K
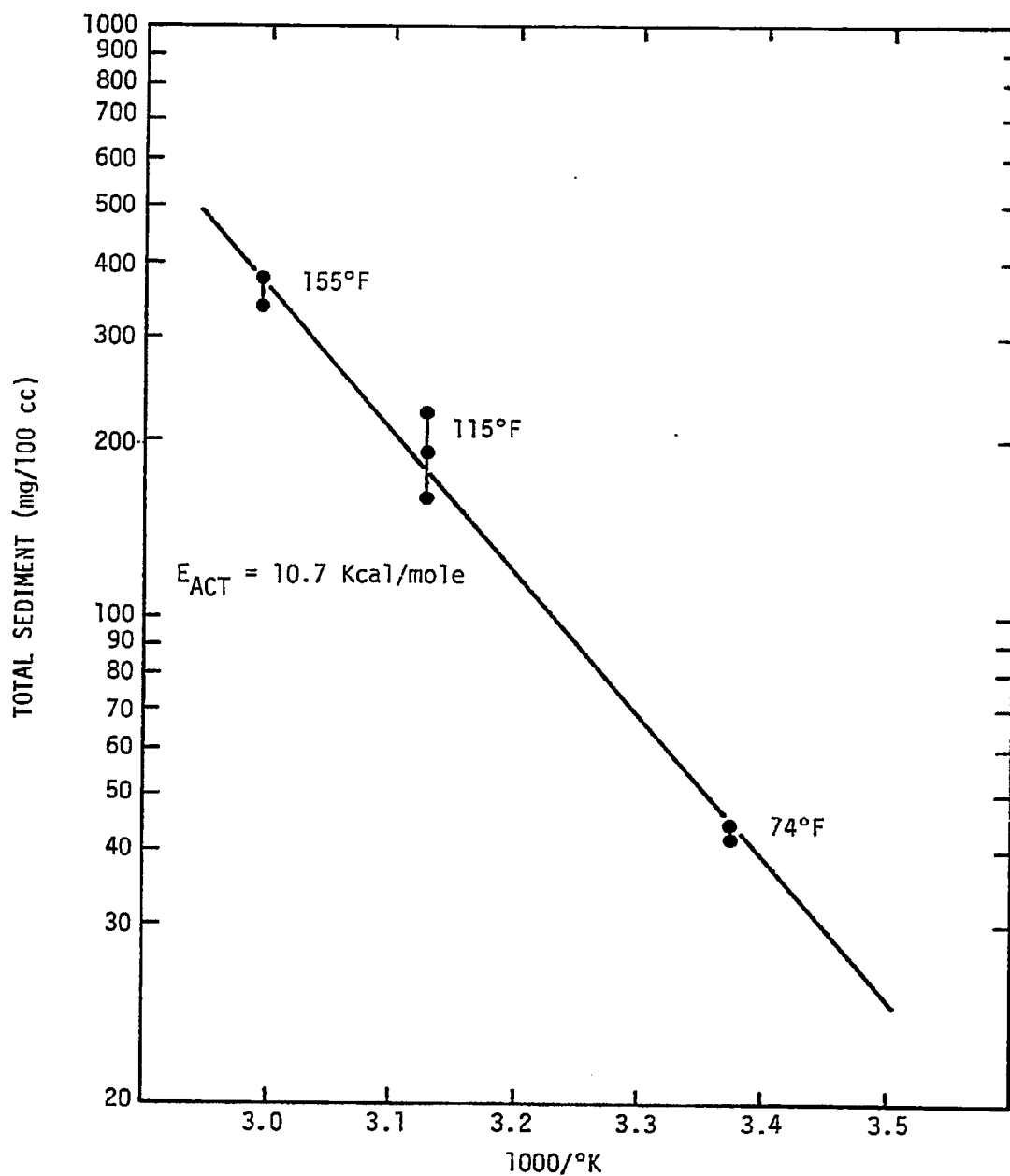
FIGURE 15

Arrhenius Plot DMP (1500 ppm N) in JP-8 14-Days

$E_{ACT} = 14.4$ Kcal/Mole
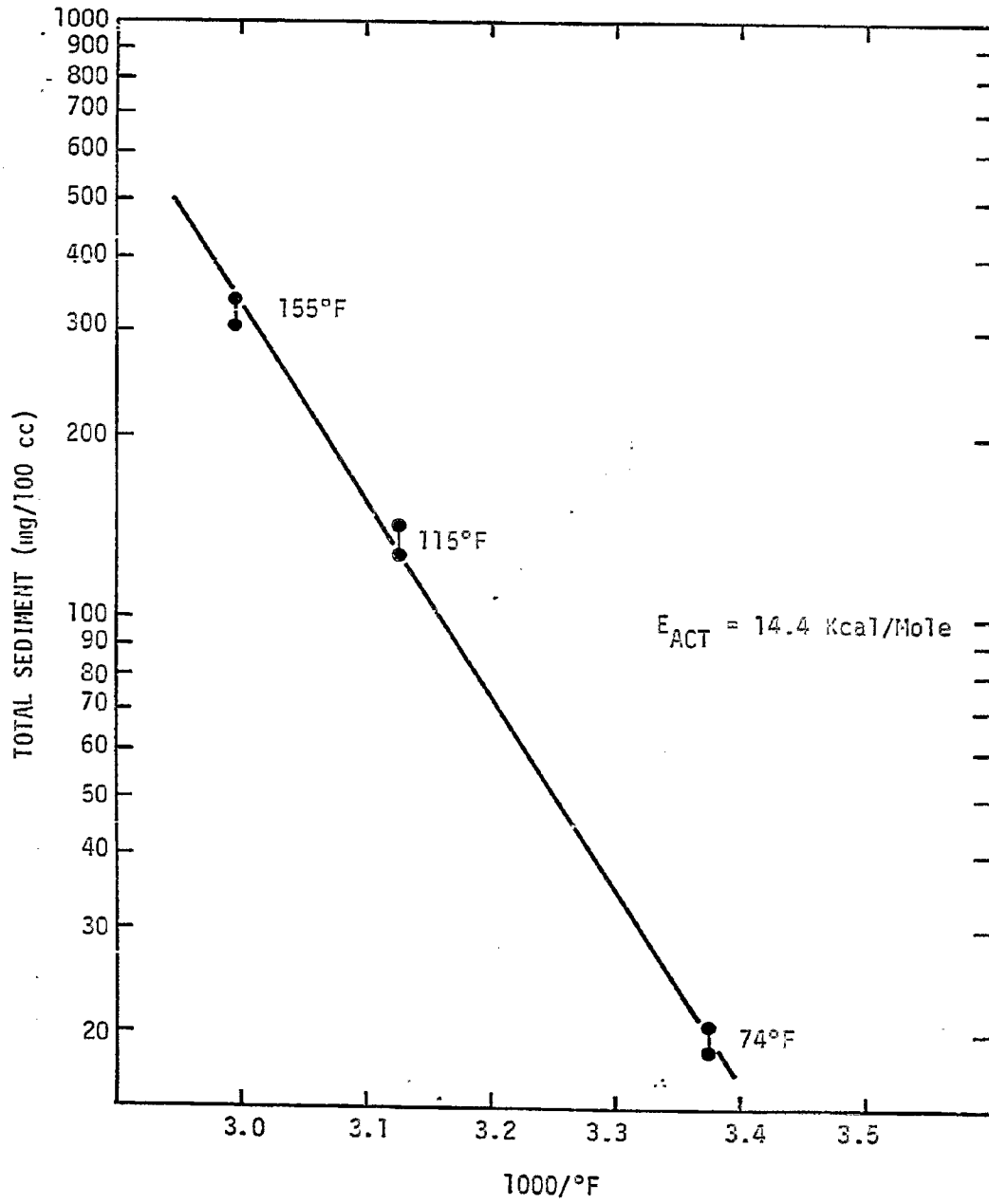
of the apparent activation energy of the reaction from the equation:[23]

$$\ln V_T - \ln V_{T_o} = \frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right)$$

where V_T and V_{T_o} are the amounts of sediment formed at temperature T and temperature T_o, E is the activation energy and R is the ideal gas constant. From the plots in Figures 14 and 15, apparent activation energies for sediment formation:

$$E_{ACT} = 10.7 \text{ Kcal/mole in No. 2 Diesel}$$

$$E_{ACT} = 14.4 \text{ Kcal/mole in JP-8}$$

are obtained. These are rather low for most organic reactions, but are similar to those obtained previously for jet fuel deposit formation rates at high temperature.[84]

2.8 EFFECTS OF DISSOLVED OXYGEN

The characteristics of the sediments[34,35] suggest that the reaction involves oxidative self-condensation. Thus, the dissolved oxygen content may play a significant role on the rate and extent of the sediment formation. Experiments are under way to investigate this. The preliminary (14 day) results of this set are shown in Table 24. These early data indicate a large effect due to dissolved oxygen content. It is interesting that sparging with air every few days resulted in no increase in deposits over the usual accelerated storage test (compare Table 12, Section 2.4.2). Clearly the "normal" tests are not oxygen limited. Longer term studies on the oxygen effect are underway.

TABLE 24

Effects of Dissolved Oxygen Content on Sediment
Formation with DMP in No. 2 Diesel[a]

Replicate	Sediment (mg/100 cc)[b]							
	Nitrogen Sparged (~1 ppm O_2)				Air Saturated (~70 ppm O_2)			
	Insol	Adherent	Total	Ave. Total	Insol	Adherent	Total	Ave. Total
1	0.6	0.6	1.2		49.1	10.2	59.3	
2	1.0	1.3	2.3		46.9	21.9	68.8	
3	0.5	0.6	1.1	1.5	46.0	32.0	78.0	68.7

(a) DMP (2,5-dimethylpyrrole) added at 750 ppm N level.

(b) After 14 days storage at 110^OF.

3. CONCLUSIONS AND RECOMMENDATIONS

Based upon the results described above, the following conclusions can be drawn:

1. Removal of all nitrogen compounds from alternate fuel sources is not required for acceptable storage stability.

- Alkylated pyrroles and indoles, especially with more than one alkyl group, are most deleterious; other N compounds are much less harmful.

- These observations could form the basis for the development of new processing approaches which could reduce the hydrogen consumption and energy requirements of shale and coal processing.

2. The nature of the hydrocarbon diluent has a lesser but still significant effect on storage stability.

- Sediment formation increases as the diluent becomes more complex in the order, n-decane < JP-8 < No. 2 diesel fuel.

- The reasons for these differences may be due to the hydrocarbon contents of the fuels (e.g. solvent effects) or to the influence of trace impurities.

3. Most oxygen and sulfur containing compounds do not produce sediment by themselves but may influence the sediment forming reactions of nitrogen compounds.

- Organic acids can be deleterious to storage stability by promoting nitrogenous sediment formation; the magnitude of the effect depends on the nature of the diluent.

- Sulfonic acids can produce sediment by themselves
  and may catalyze sludge formation with nitrogen com-
  pounds.

- Some compounds, especially some thiols,
  tend to inhibit nitrogenous sediment formation.

4. Interactions between nitrogen trace impurities can exert a
   significant effect on sediment formation.

   - "Non-deleterious" nitrogen containing species such as
     amines can interact with other nitrogen compounds to either
     promote or inhibit sediment formation.

5. The sediment forming reaction appears to be a simple oxidative
condensation of the nitrogen compound to give low molecular weight oligo-
mers. The activation energy for the reaction is low, ranging from 10-15
Kcal/mole. As expected, the reaction appears quite dependent on the
amount of dissolved oxygen in the fuel, at least in No. 2 diesel fuel.

In order to confirm and extend these conclusions, the following
additional research is recommended:

1. Continued systematic investigation of nitrogen compounds to
determine which types are deleterious and which are not. Synthesis work
will be needed to prepare compounds not commercially available.

2. Expanded investigation of N-N, N-O, and N-S interactions in-
cluding a study of the effects of oxidation state of sulfur compounds
found in oil shale and coal.

3. Expanded study of hydrocarbon types to include reactive ole-
fins and diolefins.

4. Studies of storage conditions including:

- Metal surface effects

- Dissolved metal effects

- Influence of moisture

- Effects of fuel additives

- Effects of mineral acids

5. Stability studies with actual shale and coal liquids. This is needed to extend findings in model systems to actual synthetic fuels.

6. Studies of sediment structure and further elucidation of mechanism of formation. This should be carried out both with model systems and on sediments obtained from actual coal and shale liquids.

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APPENDIX

I. COMPILATION OF PERTINENT LITERATURE REFERENCES

A. Composition of Oil Shale and Shale Liquids

B. Shale Oil Refining and Processing

C. Stability and Combustion Characteristics of Nitrogen Containing Liquids

D. Nitrogen Compounds in Coal Liquids and Their Effects on Stability

E. Methods of Analysis

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*Includes pertinent methods for measurement of storage stability, thermal stability and separation and identification of nitrogen compounds from various fuel sources.

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